TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

KHASHAYAR KHANLARI

Design of experiment of a novel cermet coating sprayed with the HVAF technology

Master of Science thesis

Examiner: prof. Petri Vuoristo and Dr. Heli Koivuluoto
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ABSTRACT

KHASHAYAR KHANLARI
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Coating as a cover applied on the surface of the substrate can have different functional and engineering applications and purposes. There are so many different techniques for making coatings including thermal spraying, laser cladding, physical vapor deposition, chemical vapor deposition and etc. Each of these coating techniques is suitable for special kind of materials to be coated and each has some advantages and disadvantages.

Thermal sprayed coatings obtained by hard materials such as WC-Co, NiCr-Cr_3C_2, Ni-based and Cobalt-based powders are considered to be the best coatings to be deposited on big components that are involved in severe wear applications. This is duo to the combined effect of high thickness achievable by thermal spraying process and intrinsic mechanical behavior of these materials. Despite these mentioned properties, thermal sprayed coatings obtained by these materials have some drawbacks such as over fusion occurring at high process temperature and high cost of powder processing.

Iron-based cermet powder (70 (Fe,Cr)C / 30 FeNiCrSi) is designed with the aim of obtaining iron-based powders with the ability of competition and also solving the drawbacks of conventional powders. These thermal sprayed Fe-based coatings have been less investigated compared to WC-Co or Cr_3C_2-NiCr or Ni- and Co-based coatings.

Microstructure, micro hardness, roughness, open cell corrosion, wear and X-ray diffraction test were done on the coatings. Results show that despite using different processing factors; almost all coatings are dense and compact. In addition, coatings exhibit high hardness (around 700 HV) which is comparable with hardness of conventional coatings. Furthermore, wear rate of the coatings were drastically lower than the substrate without any deposited coating.

In this work, Design of Experiment (DoE) as a useful technique is used for gaining more increased knowledge of the processing factors and optimizing these factors to achieve the best possible desired performance of HVAF thermal sprayed coatings obtained by this iron-based cermet. It is important to note that not all the factors affected the performance in the same manner. Some had strong impacts, some medium impact. Furthermore, interaction between the factors was also studied and analyzed in this report.

PREFACE

This thesis work was carried out within the Department of Materials Science at Tampere University of Technology.

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I would like to dedicate my thesis to my beloved country Iran and its honorable people which wherever I am they are always in my mind and soul.

Tampere, 24.3.2015 Khashayar Khanlari

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

HVAF	High velocity air-fuel thermal spraying
FESEM	Field Emission Scanning Electron Microscopy
HVOF	High Velocity Oxy-Fuel thermal spraying
SEM	Scanning Electron Microscopy
TSC	Thermal Spray Coatings
CVD	Chemical Vapor Deposition
PVD	Physical Vapor Deposition
EP/ELSP	Electro/Electroless plating
GNP	Gross National Product
AC-HVAF	Activated combustion HVAF Spraying
APS	Atmospheric Plasma Spray
VPS	Vacuum Plasma Spray
GFA	Glass Forming Ability
DOE	Design of Experiments
FFE	Full Factorial Experiment

1. INTRODUCTION

The need to prevent wear and corrosion is an old and totally recognized problem. Both wear and corrosion limit the useful life of engineering components in different areas of industry. In fact wear and corrosion both cause in huge waste of money annually and impact each nation's economy. In just 1990 in the United States of America, 7% of the Gross National Product (GNP) was wasted on wear and corrosion.

There are, however, several different ways and tactics to withstand wear and corrosion. One direct way of combat is to construct components completely from wear- and corrosion-resistant materials, but this tactic is in fact really expensive. Since corrosion and wear start from the surface of a component, a coating approach can be effective tactic for reducing costs and maximizing life of components.

By considering performance demands and working conditions of engineering components, especially those conditions associated with combined wear and corrosion, hard coating materials seem to be the best option as materials used for coating of components. Hard materials are usually considered to have hardness values $\geq$1000 kg/mm^2. Ceramics, cermets, metal alloys are being used as engineering materials for coating to combat and withstand corrosion and wear.

There are various coating and surface modification techniques used for applying coatings, such as Thermal Spray Coatings (TSC), Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD) and Electro/Electroless plating (EP/ELSP). Choosing the coating method and coating material to withstand wear and corrosion and maximizing life of component can be hard and confusing and in most of cases depends on so many factors such as size of component, substrate material, its application, etc.

Thermal sprayed coatings obtained by hard materials such as WC-Co, Cr_3C_2-NiCr, Ni-based, Co-based powders are considered to be the best coatings to be deposited on big components that are involved in severe wear involved applications. This is duo to the combined effect of high thickness achievable by thermal spraying process and intrinsic mechanical behavior of these materials. In addition these materials are relatively noble so they are intrinsically considered to be as appropriate coating materials for resisting corrosion if they can prevent the penetration of corrosive electrolyte to the substrate.

Despite these mentioned properties, thermal sprayed coatings obtained by these materials have some drawbacks. Some of these drawbacks are the result of the thermal spraying process used and some others are the result of the used materials.

Over fusion occurring in high temperature thermal spraying processes result in undesirable thermal alterations such as decarburization, decomposition, and oxidation in powders. These problems have resulted in designing a new generation of thermal spraying processes with lower temperature and higher velocity (for compensating the lack of plasticity). High velocity oxy-fuel thermal spraying (HVOF) and high velocity air-fuel spraying (HVAF) are processes that are developed by considering this trend.

Safety of used materials is a major interest of safety regulating bodies around the world. The powders that are most probable to be dangerous are those containing high amount of nickel, cobalt, copper and chromium. Specifically these materials such as Ni- and Co-based should not be used at all in food and packaging industry because there is a high risk of product contamination. In fact these powders are potential carcinogens for humans. In addition these powders have high and fluctuating price which is not desirable.

These mentioned issues can possibly be solved by replacing these materials with Fe-based alloys. Iron is the fourth abundant element on the earth crust after oxygen, silicon, and aluminum. In fact 4.71 percent of the earth crust mass is Iron. In addition the different extraction processes of iron from iron ore are technologically well understood. These parameters (stable price, different extraction methods, and abundance) and its superior behavior when it is alloyed with other elements make this material really good candidate for different applications.

On the other hand, results of different researches exhibit that Fe-based powders although being good alternatives for electroplated chromium and some other thermal sprayed metal coatings in some specific applications, do not show comparable wear resistance with conventional cermets such as WC-Co or Cr_3C_2-NiCr.

Cermet powders with iron-based are designed with the aim of obtaining iron-based powders with the ability of competition with conventional powders. These thermal sprayed Fe-based coatings have been less investigated compared to WC-Co or Cr_3C_2-NiCr or Ni- and Co-based coatings. In this work, more investigation has been done on HVAF thermal sprayed coatings obtained by iron-based cermet.

(Fe,Cr)C-30FeNiCrSi (Amperit 575.074) novel powder was sprayed by High Velocity Air-Fuel (HVAF) method with different factors. Design of Experiment (DoE) is used for planning, designing and analyzing the experiment so that the best possible desired performance of HVAF thermal sprayed coatings can be obtained by spraying this iron-based cermet.

2. WEAR

Surface interaction controls the operation of practically every industrial developed component. Friction and wear are two main disadvantages of solid to solid contact.

Lubrication and surface modifications are two general approaches to control friction and wear. Liquid lubrication is a technological trouble because; pumps and cooling systems are needed to keep their performance. In addition they are not environmentally friendly. Therefore surface modification sounds to be the best way to control wear and friction.

Wear is the major cause of material wastage and results in degradation of components mechanical performance so minimizing wear can result in cost saving. Friction is a main cause of wear and energy dissipation. It is estimated that one-third of the world's energy resources is needed to overcome friction in different forms. [1] The huge cost of tribological deficiencies to any national economy is mostly caused by large amount of energy and material losses occurring during components operation. In 1966, it was estimated by Peter Jost that by the application of the basic principles of surface modification and tribology, the economy of U.K. could save approximately £515 annually. In the U.S.A it has been estimated that by progressing in tribology, approximately 11% of total annual energy can be saved in four major areas of transportation, turbo machinery, power generation and industrial process. [1]

Although this thesis is concerned with preventing the harmful effects of wear and corrosion, it is good to mention that corrosion and wear can also have some useful practical applications. Sanding, grinding, polishing and etching are all useful aspects of wear and corrosion phenomena. [2]

2.1 Different wear mechanisms

Wear involves the physical removal of material from the surface of a solid object. [2] Wear can be classified into four general categories of abrasive, adhesive, erosive and fatigue wear.

2.1.1 Abrasive wear

Wear by abrasion and erosion are types of wear caused by contact between a particle and solid material. Abrasive wear is the loss of material by the passage of hard particles over a surface of material. Abrasive wear happens whenever a solid object is loaded against particles of a material that have equal or greater hardness compared to the ob-

ject. As an example of this type of wear is the wear of shovels on earth-moving machinery. Cutting, fracture, fatigue and grain pull-out are different mechanisms of abrasive wear involved during abrasion. During abrasive wear the particles or grits may remove material from the surface of component by microcutting, microfracture, pull-out of individual grains or fatigue by repeated deformations. [1]

During cutting, the sharp grit or hard asperity cuts the softer surface. The material that is cut is removed as wear debris. Fracture of the worn surface happens when the abraded material is brittle. Grain detachment or grain pull-out occurs when the boundary between grains is relatively weak. In this case the entire grain is lost as wear debris.

Abrasive wear happens in two modes, two-body abrasive wear and three-body abrasive wear. In three-body abrasive wear the grits are free to roll and slide over the surface because they are not held rigidly.

Hardness has a key role in preventing abrasive wear and it is generally said that hard materials have slower wear rates compared to softer materials. The basic method of abrasive wear control is to raise the hardness of the worn surface until its hardness is at least 0.8 of the grit hardness. It should be considered that by increasing hardness, the material would become more brittle and it shows that there is a limit in minimizing abrasive wear by just increasing the hardness of material. Because when the material becomes so brittle then abrasive wear can happen by fracture mechanism however the cutting mechanism is minimized as the result of high hardness. [1] When temperature, humidity, aggressiveness of the environment (corrosion) increases the abrasive wear phenomena is promoted. It should be emphasized that abrasion wear represents more than 50% of wear. [3]

2.1.2 Erosive wear

Erosive wear is caused by the impact of particles of solid or liquid against the surface of an object. Damage to gas turbine blades when an aircraft flies through dust clouds exemplifies this type of wear. Erosive wear involves several wear mechanisms which are largely controlled by the particle material, the angle of impingement, and the impact velocity and particle size. Maybe the relation between impingement angle and the corresponding wear behavior that different materials show in different angles can be a good way to classify different materials during this type of wear. Impingement angles can range from 0° to 90°. At zero impingement angle there is negligible wear because the eroding particles do not hit the surface. At small impingement angles of about 20°, intense wear may occur if the particles are hard and the surface is soft. Wear mechanism is in this condition similar to abrasive wear. But if the surface is hard and brittle the intensive wear happens in bigger angles and wear rate would be maximum at impact angles near 90°. The relationship between wear rate and impingement angle for ductile and hard brittle materials is represented Figure 1.

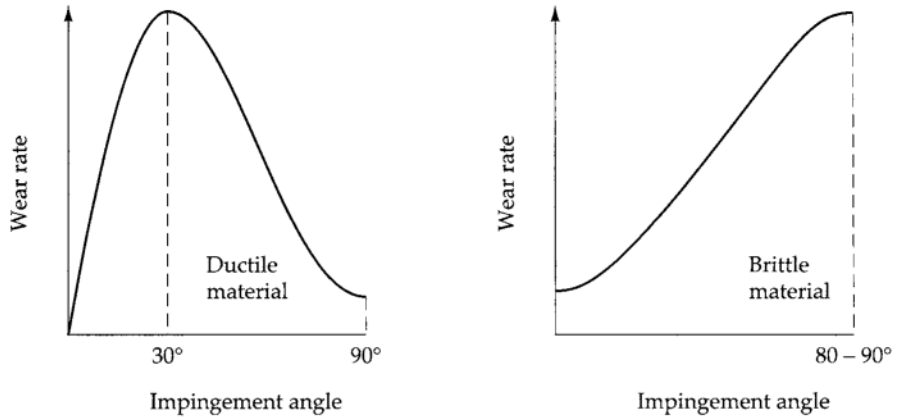


Figure 1: Schematic representation of the effect of impingement angle on wear rates of ductile and brittle materials. [1]

Materials with high hardness and toughness can be good candidates for combating erosive wear. In low angles of impingement, materials with high hardness and potential for work hardening can be so effective. However it is found that improvement in mechanical behavior doesn't necessarily result in superior resistance to erosive wear. In fact if the material is too brittle then fracture can happen in high loads especially in high impingement angles.

2.1.3 Adhesive wear

Friction and adhesive wear occurs when particles are transferred from one interacting surface to the other. When different materials are in contact, particles would transfer from the softer material onto the harder one. This type of wear is promoted by increasing the load and/or temperature, and under dry friction condition, or poor lubrication. This type of wear depends on different factors such as structure, composition, hardness and melting temperature of the material. [3]

Adhesive wear is a very serious form of wear that results in instability in friction coefficient. In this type of wear sliding contacts can rapidly be destroyed and even in severe conditions of wear sliding motion may be prevented as the result of large coefficients of friction. In some cases, transferred particles as a consequence of adhesive wear can even jam the sliding contacts. [1]

A tendency for all materials to mutually adhere when brought into a close contact is the basic cause of adhesive wear. In metals this tendency can be explained by electron transfer between containing surfaces. So many free electrons are present in metals and during contact these electrons may exchange between the two solids and make bonding.

In addition some degree of plastic deformation between asperities is necessary for true contact to be established when two surface are in contact. Hexagonal close-packed metals have so fewer slip systems than body-centered metals and body-centered metals have less slip systems than face-centered materials. As a result hexagonal close-packed metals are less ductile than body-centered metals and body-centered metals are less ductile than face-centered metals, which results in lower adhesion of hexagonal close-packed metals and body-centered metals compared to face-centered ones. In a way ductility of material result in more probability and tendency of true contact establishment compared to brittle material and in another way ductile materials have higher tendency to accommodate the applied load between established contacts by deformation that happen in shear bands. When each shear band reaches a certain limit, a crack is initiated. The crack extends across the asperity and finally it results in particle detachment. Contacting asperities of brittle materials break away with little deformation and fewer particles are produced compared to ductile materials. Seizure and scuffing are two sever types of adhesive wear that can occur in mechanical contacts when there is absence of lubrication. Plain bearings and gear teeth are prone to this problem. [1]

To reduce this type of wear, dry friction between materials that contact each other should be avoided or coatings containing solid lubricants must be used. Compatibility of materials is also an important factor. Couple of materials rubbing on each other should be chosen in a way to have low adhesion and friction coefficient. The roughness of contacting surfaces should be as low as possible to prevent contact establishment. [3] Load is another factor which influences the adhesion between asperities during contact. Load can result in plastic flow and as a result establishment of true contact between surfaces and increase in friction coefficient and adhesion. Oxidation of metal surfaces can lower adhesion to acceptable levels by reducing the tendency of contacts to adhere with each other. [1]

2.1.4 Fatigue wear

Surface fatigue wear is the result of cyclic loading in contacts, with stresses induced by rolling, shocks or sliding. This kind of wear depends on material properties such as: structure, cohesion, elastic limit, toughness and residual stresses. The worst kind of fatigue wear occurs when crack propagates after crack initiation, it happens mostly in brittle materials. The best materials to be used are hard ones with high toughness. The surface needs to be smooth with no irregularities because irregularities are potential places for crack initiation. [3]

2.2 Wear resistant surface treatments and technologies

In order to be competitive in the market, it is important to be able to produce surfaces that are highly resistant to wear and corrosion and retain their intended mechanical, electrical, optical or thermal properties for a long time. Surface treatments and technologies have an outstanding role to play in this respect. Needs for surface treatments and technologies can be summarized by the following:

(1) Improving functional and operational performance by, e.g., making higher temperature exposure possible by the use of thermal barrier coatings.

(2) Improve component life by minimizing wear and corrosion

(3) Reduce component cost by using a low cost material with an expensive coating

The most important surface treatments to be cited are: strain hardening, surface hardening and thermochemical treatments. All these methods result in modification of surface without any extra layer added to surface of substrate. In contradict; coating technologies result in better property of substrate by depositing an extra layer on the surface of main substrate material which is quite different and independent from substrate material. Electro/Electroless plating, Chemical vapour deposition, Physical vapour deposition and thermal spraying are four methods to deposit coatings.

Selection of a coating-material and coating-process for a specific substrate can be complicated and a hard task. Coating material should be chosen in a way to be appropriate and satisfactory for both corrosion and wear. The best way to be certain and sure about the chosen material is to examine the damaged surface for understanding and revealing the degrading mechanism, this can show the surface properties that are required to give a satisfactory property. In this case the appropriate coating material and process can be chosen. Selection of coating materials can be in most of the cases so difficult . For example consider a specific application which both hardness and toughness should be combined simultaneously. The final properties of the coated surface are the result of the combination of the coating material used and also the coating-process that is used to deposit coating. These include different properties such as adherence, thickness, uniformity, residual stress, porosity, density, surface roughness, microstructure and composition. Coated surface property needed for wear phenomena can be totally different from that needed for corrosion phenomena. It is important to consider that in so many applications corrosion and wear can happen together, in this case the best coated surface solution is often a smart compromise in choosing both the coating material and coating process. Finally it should always be kept in mind that finally the most important factor

on a production scale is the economic considerations of both the coating process and the coating material. [2]

2.2.1 Strain hardening

In strain hardening, plastic deformation processes are applied on materials. These plastic deformations can be applied either prior to the application by processes like rolling and impact loading, peening or can be applied during service life. The depth of hardening can vary from 1 mm for rolling to as high as 20 mm for impact loading. [3]

2.2.2 Surface hardening

Surface hardening can be achieved by heating the surface of material with flame, induction, high-frequency resistance, plasma, laser, and electron beam. By using these thermal treatments, hardenable grades of steel are heated to reach the austenitizing temperature and then they are cooled faster than the critical cooling rate of the steel to obtain hard phase on surface. The depth of hardened layer is between 0.5 to 5 mm. [3]

2.2.3 Thermochemical treatments

Chemical elements such as, carbon, nitrogen, niobium, boron or vanadium are diffused into surface of material at elevated temperatures to form for example very hard carbon layers on surface of material. Carburizing, carbonitriding, nitriding, nitrocarburizing, and boriding are between the different treatments that can be applied. In the normal carburizing treatment the thickness of the carburized area is $x\ (mm) = 0.635\sqrt{t}$, where t is the treatment time in hours. [3]

2.2.4 Electro/Electroless plating

Electrochemical treatments: In electroplating a coating is electrodeposited on an electrode which is the part that is going to be coated, this part is in most of the times cathode. Metals and alloys are deposited that way. [3]

Chemical treatments: In electroless plating, chemical reducing agents are used instead of the electric current for reducing the ionic state material in its solution and depositing it. [3]

Hot dip coatings: The parts that are supposed to be coated are dipped into a molten bath of coating material. Low melting temperature materials like zinc and aluminum that are going to be used for corrosion protection are coated in this way.[3]

Thickness of coatings obtained by these methods are between 10 µm to 1 mm. Maybe the most important advantages of these methods are that they are omnidirectional and the substrate is kept at low temperature and their cost is low. [3]

2.2.5 Chemical Vapor deposition

Chemical vapor deposition (CVD) processes generally involve thermally activated chemical reaction or decomposition of gas precursors to obtain uniform and dense coatings on substrate surfaces. The surfaces are heated and are contained within an enclosed container. [2] Coatings are obtained from the gaseous or vapor state. The coating results from the decomposition of chlorides, fluorides, bromides, iodides, hydrocarbons, phosphorus, and ammonia complexes. The gaseous precursor is thermally decomposed and in this way the coating is produced on the component surface. Usually CVD coating thicknesses are below 50 µm. [3]

2.2.6 Physical Vapor Deposition

Physical vapor deposition (PVD) is used to apply coatings by condensation of vapors in a vacuum. PVD technique generally refers to three generic coating methods that involve evaporation, ion plating or sputtering.

In evaporation, vapors that are produced by heating a solid by different means such as, direct resistance, laser, electron beam, and etc. are condensed onto the substrate surface. In sputtering the particles are ejected from the target and then collide with substrate and create adherent and dense coatings. In ion plating, ions are extracted and accelerated from an ion source. Then the ions are drifted through a field free space to reach the substrate. PVD coating thickness is usually less than 5 µm. [3]

2.2.7 Thermal spraying

Thermal spraying is the most versatile process of coating material deposition. During this process the coating material is molten or semi-molten in a heating zone. The molten particles are accelerated towards the substrate and then cooled to form the coating. The cooled particles are bonded to the substrate by mechanical interlocking. There are different methods to melt the particles and propel them toward the substrate and the most common ones are flame spraying, detonation gun spraying, plasma spraying, High velocity oxy-fuel spraying, high velocity air-fuel spraying, etc. Coatings with thickness of 50 µm till 6.35 mm and even thicker are possible to be deposited by this method. [1] Till today the major use of thermal sprayed coatings in the USA has been for applications in gas-turbine engines for both aerospace and stationary industrial demands. These applications include thermal sprayed coatings of carbide cermets such as WC-Co and

Cr_3C_2-NiCr onto the midspan shroud of turbine blades and coatings of nitride, oxide, and carbide cermets on blade tips of compressor rotors. [2]

2.2.8 Advantages and disadvantages of different surface treatments and technologies

Hard materials which are intended to give prolonged protection against wear are usually used as material for wear resistant coatings. Adhesive wear and abrasive wear are often reduced by using these coatings due to their high hardness. There are numerous methods of depositing hard coatings.

Applications of wear resistant coatings are found in every industry, for example mining excavator shovels and crushers, cutting and forming tools, rolling bearings in liquefied natural gas pumps, etc. In most of these applications wear is a critical problem. Many of hard coating materials are so expensive so it is not beneficial to make the entire component from them. A really important benefit of hard-coating technology is that cheap and light substrate like, steel or aluminum can be coated by an exotic high performance and wear resistant material. There are many different methods of applying wear resistant or hard coatings.

The wear resistance of a surface can be improved by thermal hardening or by introducing alloying elements, e.g., carburizing or boriding. These methods suffer from the disadvantage that the substrate needs to be heated to relatively high temperatures. Moreover, these methods are applied for small components but not large components, like, large shafts or turbine blades or blades of compressor rotors, because these methods mostly need vacuum and chamber for their processing. Studies of wear resistant coatings reveal that thick hard coatings are most effective in suppressing and controlling different types of wear. By considering the above mentioned points one can easily understand that thermal spraying is the most versatile method for depositing thick hard coatings on large components. [1]

CVD is especially useful for depositing hard, refractory materials, from ceramics to metal alloys and intermetallics to carbon and diamond, onto substrate surfaces. Since most CVD techniques do not require high-vacuum system configurations, equipment costs are relatively low. In addition CVD is an interesting method because it is omnidirectional coating process that has potential to produce dense, uniform, and high adhesion strength coatings with controlled microstructure. The main disadvantage of CVD is that this process occurs in high temperature and this matter limits the choice of substrate material. In addition it makes this process hard for depositing coating on large components. [2]

PVD is a really versatile process since most of the materials are possible to be coated by this method. Both amorphous and crystalline microstructures are feasible to be coated

by this method and under controlled conditions good adherence is achievable. The primary disadvantage is that due to high vacuum needed this process requires the most expensive equipment among all other methods. Like thermal spraying PVD methods are line of sight and it can result in non uniform coatings when the substrate has complex shape. [2]

Both PVD and CVD are used for depositing thin coatings and precision components. The thickness obtained by PVD and CVD vary between 0.5 to 10 μm. In addition these processes need enclosure in vacuum or low pressure so large components cannot be treated by them.

The largest commercial uses of electro/electroless plating have been for decorative purposes, and wear and corrosion protection have had lesser usages. According to Scwarts et al. only ten single-metal elements are used today in large scale production in electroplating method. These include Cr, Ni, Zn, Rh, Ag, Cd, Sn, Au, and Pb. Chromium is the only metal among all these mentioned metals that shows a hardness above 1000 HV so it can be used as wear resistance coating. [2]

Chromium plating results in release of carcinogenic Cr^{6+} during the deposition. This matter has resulted in so many efforts and investments for finding other processes and materials to substitute electroplated chromium but with similar wear resistant property. Thermal sprayed cermets including WC-Co and Cr_3C_2-NiCr display even superior behavior compared to electroplated chromium. [7-12]

2.3 Wear resistant materials

Ceramic materials are generally extremely hard and therefore should have good abrasive wear resistance. Alumina is an example of a hard ceramic mineral which has Mohs hardness of 9 if it is the form of corundum. [1] Ceramics such as Al_2O_3 , Al_2O_3-13%TiO_2, Cr_2O_3 are good candidates for resisting against adhesive wear. WC-Co, WC-Co-Cr, Cr_3C_2-NiCr cermets show really good wear resistance under adhesive wear conditions. Hard ceramic coatings of oxides, carbides, nitrides, and borides are appropriate for abrasive and adhesive wear applications that do not involve great impact or cyclic loading. But cyclic loading is an inevitable part of most of the mechanical applications. For these applications metal-bonded ceramic materials or cermets are appropriate. The role of metal matrix is providing toughness or ductility while the dispersed hard brittle carbide particles provide wear resistant against abrasive and adhesive wear. [2] WC-12%Co,WC-17%Co, Cr_3C_2-NiCr, Cr_3C_2-NiCr are different cermets used for combating different types of fatigue wear.[3]

The metallic hard alloys are also used for wear protection applications. In these materials, the metalloids carbon, boron, and silicon form together with chromium (also for corrosion protection), tungsten, molybdenum, and vanadium, homogeneously dispersed hard phases in a ductile matrix which is eutecticly solidified. Ni-based, Co-based, and Fe-based are some examples of hard metallic alloys. In Ni-based, and Co-based hard metallic alloys, addition of boron and silicon results in self fluxing property. Self-fluxing alloys such as Co-Cr-W-B-Si and Ni-Cr-Si-B are some examples of these systems. CoMoSi (Tribaloy) is another system which has friction and wear applications. The mechanism of their hardness is based on generation of hard, intermetallic laves-phases embedded in a ductile matrix. [2]

These metallic hard alloy materials show generally excellent corrosion resistance but their hardness is not particularly high so they cannot compete with cermets for sever wear resistance. To compensate this they can be sprayed with hard particles or they can be heat treated.

3. CORROSION

Corrosion can be regarded as a chemical degradation of material by its surrounding environment. It is a kind of chemical material-removal process from the surface of material that is generally undesirable. [2] Decrease in mechanical properties, impairment in surface quality (hardness and roughness), weight change, changes in dimensions, leaks in containers, change in appearance of material, economic losses, damage to environment, safety risks are all undesirable effects of corrosion.

In corrosion process materials loss occurs through electrochemical or chemical reaction with the surrounding medium. At high temperatures corrosion reactions are oxidation, carburization, nitriding, sulfidation, and molten-salt corrosion. [3]

The dissolution of metallic elements by the formation of ions by electron loss is corresponding to anodic reactions and can be written as

$$M\ (metal) \rightarrow nM^{+} + ne^{-}$$

Where M is a metal, Mn^{+} is a positive ion, and e- is an electron. This electron loss lets the metal ion to bond to other groups of atoms that have negative charge. Steel rusting where water (H_2O) and oxygen (O_2) are involved can be considered as an example:

$$Fe \rightarrow Fe^{2++}\ 2e^{-}$$

The free electrons that are produced will participate in a cathodic reaction and react with water and oxygen:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

both reactions can be combined and written as:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

Since O_2 dissolves rapidly in water and because there is generally an excess of it, dissolved O_2 will react with iron hydroxide to make the hydrate iron oxide, $2Fe_2O_3.H_2O$, which is called brown rust.

$4Fe(OH)_2 + O_2 \rightarrow 2H_2O + 2Fe_2O_3.H_2O$

It is understandable from these equations that the corrosion rate is connected to electrons production, corresponding to a corrosion current flow. It should be mentioned that the presence of an impervious oxide layer on the surface of metal would behave as barrier and can prevent the corrosion and in this case the metal is said to be passivated. In fact apparent corrosion rates may decrease as these protective scales form on the surface of the substrate; this is a kind of self-limiting effect of corrosion. [3]

Corrosion rate equation is expressed by

$$C_T = C_0 (\Delta G^*/RT) \qquad (1)$$

Where C_T is the corrosion rate at temperature T(K), generally expressed in mm/year or mpy, C_0 is the rate at 0 K, R is the ideal or universal gas constant, and ΔG^* is the activation energy of the corrosion reaction.

$$E-E_c = \beta(\text{Log } I)/(\text{Log } I_c) \qquad (2)$$

The above equation is the transformed form of equation (1) in logarithmic form. The energy terms are considered as potentials and rates as currents. In the above equation, E is the measured potential of the specimen when current flows, E_c is the corrosion potential (no current flowing), I is the impressed current, I_c is the corrosion current (no external current), and β is a constant. [3]

3.1 Different corrosion mechanisms

General corrosion, galvanic corrosion, intergranular corrosion, pitting corrosion and transgranular corrosion are different types of corrosive attack that commonly occur in coatings. [3]

General corrosion corresponds to 30% of failures caused by corrosive attack. In this type of corrosion, the average rate of corrosion on the surface is uniform. Galvanic corrosion, pitting corrosion, intergranular and transgranular corrosion are localized types of corrosion which are responsible for 70% of failure cases caused by corrosive attack. Surface damage is intensified whenever localized type of corrosion occurs. Applied stress and fatigue can boost the localized effect. [3]

Galvanic corrosion occurs when two dissimilar metals are in contact with each other in a conductive solution. In this case the more anodic metal corrodes, while the more cathodic one would be protected from corrosion. Coating is prone to intergranular corrosion when a chemical element is depleted in the coating grain structure during fore ex-

ample heat treatment. Pitting is a localized type of corrosion that results in pit formation on the surface of material. The pit cavities can be kind of stress raisers. If the coating is under high static tensile stress surrounded by corrosive environment then transgranular corrosion can occur. In this type of corrosion, intergranular or transgranular cracking occurs based on coating material and its microstructure. [3] In fact some solid materials are susceptible to cracking, whenever the surface of the solid is exposed simultaneously to a corrosive environment and an applied stress. If variable repeated loads or stresses are involved, the phenomenon is called corrosion fatigue. Corrosion fatigue can result in catastrophic failure of components. [2]

3.2 Corrosion behavior of material, influence of material and environment

Corrosion behavior of material can be affected by two general factors: material characteristics and environmental characteristics.

Inherent reactivity of material (based on EMF series), tendency to form insoluble corrosion products (passivity), and metallurgy of material are different material characteristics that control corrosion behavior of material. Metallurgy of material includes microstructure, crystallographic nature, grain boundaries, composition, and defects in material. Materials always have imperfections know as defects such as, point defects (vacancies, subtitutional atoms, interstitial atoms), line defects (edge dislocations, screw dislocations), volume defects (voids, cracks) in their structure and these often have a noticeable effect on their corrosion properties.

Temperature, pH, pressure and flow rate are different environmental factors that may have considerable effects on corrosion behavior of material. Increase in temperature results in higher severity of corrosion. Change in pH can change the nature of coatings reaction. Coating can display immune, active or passive behavior in different pH of environment and it can be understood based on potential-pH diagram. In addition, in acidic environments, coatings tend to degrade and in alkaline environments, delamination of coating is probable. Changing pH, O_2 concentration and humidity are some tactics to control the environment.

Material and environment should be optimized to inhibit corrosion and display controlled rate and form of corrosion. All the above mentioned factors related to material and environmental characteristics should be considered and optimized for controlling corrosion. In addition, design of system is also an important issue for preventing catastrophic corrosion. Finally it should be considered that in fact it is not an easy task to choose material and optimize environment in a way to be effective for corrosion protection and in most of the cases the environmental parameters are not in our control. In these conditions choosing and processing a specific material with optimized properties

for being appropriate to be used in that environment is not possible or if it is possible then it would be so expensive.

Coating technology and surface modification can be a solution for this problem. Coatings applied to metal surfaces can be really effective for inhibiting corrosion in several applications. As it is already mentioned, corrosion behavior of a specific coating material in specific environmental parameters depends on inherent reactivity, tendency to form insoluble corrosion products and metallurgy of coating.

3.2.1 Types of coatings to resist corrosion

Based on inherent reactivity of coating material, coatings can be divided to two general branches of anodic and cathodic coatings, compared to substrate material.

If in a specific environment, coating material is anodic compared to substrate material then coating would sacrifice itself when coating and substrate are in direct contact with corrosive solutions. In these conditions existence of defects such as cracks or voids which result in penetration of corrosive medium to substrate are not in great concern because anyway coating would scarify itself and substrate is going to be protected. Galvanized coatings protect substrate material in this way. This type of coatings are extremely effective in applications where just corrosion is involved but not in applications where corrosion and wear are combined together because they do not show high hardness which is necessary to protect them against wear.

On the other hand if coating material is nobler than substrate material then coating processing has a significant importance for corrosion prevention. Defects such as voids, porosities and cracks which result in corrosive penetration to substrate should be eliminated and prevented to form during coating processing otherwise substrate may corrode with high rate and coating would be useless. In practice, it becomes increasingly expensive to achieve fewer and fewer defects because it needs a really high precise control over processing parameters. Bond coating, sealing, and post heat treatments are practical solutions applied on these coatings to prevent corrosive solution to penetrate coating and in fact insulate coatings. In addition the coating material is expected to display low corrosion rate and even passivation in that specific environmental condition that it is going to be used so it does not corrode away. Most of the hard coatings such as Cermets, austenitic stainless steels, Ni-base alloys, Co-base alloys, and etc. are among this type of coating while carbon steel is used as substrate. This type of coating materials are used in applications where corrosion and wear (corrosive wear) are combined together since these coating materials display high hardness. Thermal spraying is probably the most versatile method for depositing thick layers of these materials onto substrate.

3.3 Role and importance of thermal spraying and hard coatings to resist combined effect of corrosion and wear

Corrosive wear occurs when corrosion and wear occur simultaneously and effects of corrosion and wear are combined. This results in a more rapid degradation and damage to the surface of material and coating. A surface that is corroded or oxidized may be mechanically weakened and in this case they can wear at an increased rate. [3] Erosion corrosion, cavitation damage, and impingement attack are different examples of combined effect of corrosion and wear. Many corrosion resistant coatings that are not considered to be hard are quite effective in applications where wear is not involved but if wear is also a concern in that specific application then coatings should be chosen in smart way to combat both wear and corrosion.

Austenitic stainless steels, nickel-base alloys, cobalt-base alloys, cermets with WC, Cr_3C_2 are used against corrosion associated with wear. As an example, NiMo (Hastelloy system) is used for corrosion protection applications and molybdenum improves the performance of nickel. [3]

Cermets are used for applications where sever wear is involved like in oil and gas industry. The corrosion resistance of cermets can be improved by the smart and proper choice of binder material. WC-CrNi is an example of cermet material which shows passive behavior, as stainless steel, when exposed to see water. Cr_3C_2-NiCr is another cermet coating which displays good and acceptable sliding wear in sodium chloride solutions. [3]

As it is mentioned already, these types of non-sacrificial coatings will never protect the substrate if connected porosities, voids and cracks exist in coating. Bond coating, sealing, and post heat treatments are practical solutions applied on these coatings to prevent corrosive solution to penetrate coating. Thermal spraying is probably the most versatile method to deposit thick layers of these non-sacrificial coatings onto substrate of big components for applications where corrosion and severe where are both involved.

4. THERMAL SPRAYING TECHNOLOGY

Thermal spray coating as a line of sight coating technology, offers several different methods to deposit relatively thick coatings. The possible thickness which can be achieved by these methods varies between 50 microns to 6.35 mm or even thicker. Thermal spraying is a really versatile method to deposit almost any material, from plastics and polymers, to ceramic and metals. Withstanding melting without decomposition is the only requirement for materials to be used by thermal spraying method. As it is concluded in previous parts, thick hard coatings are used in applications where corrosion and severe wear are both combined simultaneously. Thermal spraying is indeed a really good candidate for depositing relatively thick layers of hard coatings. [2-3]

The earliest documents for thermal spraying are referred to Swiss engineer M. U. Schoop; these patents originate in the early 1900s. At first, welding torch was used to melt lead and tin wires; the heat was generated from the energy of acetylene/oxygen flame. Later the torches were evolved so they could use powdered materials. In 1908, Mr. Schoop patented the wire-arc spraying, after this the deposition of various types of metals became possible. The requirement for new materials in different strategic industries such as aeronautical and space industries caused a rapid development of thermal spray technologies in 1960s. The thermal spraying technologies developed more in the 70s by employment of thermal plasmas, after this time depositing high melting temperature materials like refractory materials became possible. Since 80s the major developments in thermal spraying are focused to increase particle velocities. [2] The trends is focused to extend the process conditions which result in higher particle velocity and lower temperature. Introduction of High velocity oxy-fuel processes, High velocity air-fuel processes, and cold spraying are all in this way. These days the use of thermal sprayed coatings is spread to more and more industries, and the requirements for improved quality of coatings have led to huge research and developments activities. Wear resistant coatings, corrosion resistant coatings, thermal insulation coatings, electrically conductive coatings, electrically resistive or insulating coatings, electrochemical active coatings, dimensional restoration coatings, etc. are different applications of thermal spraying. Aerospace, land-based turbines, automotive, power train components, electrical and electronic industries, medical industry, Marine base structures, etc., are different areas where thermal sprayed coatings have applications. [3] The results of a research show that approximately 15 pounds of ceramic and cermet hard coatings deposited by thermal spraying processes can be found in a typical modern jet-aircraft engine. [2]

During thermal spraying, a solid coating material (powder, wire, or rod form) is inserted into a chamber with high enthalpy. In this high enthalpy chamber, the solid coating ma-

terial is converted into molten or semi molten state with high plasticity. In fact, while the particles are accelerated in a high enthalpy gas jet (flame, plasma), they are simultaneously heated up, and based on their dwell time, average particle size distribution, and temperature distribution through the jet, they become partly or totally molten. During the flight, the particles may interact with the surrounding medium and molten or semi molten particles may oxidize. Due to high temperature, plasticity and velocity of impacting particles, after impingement to the substrate, they become flattened, fractured, spread, and quenched within a very short period of time and indeed they form splats. The necessary time for solidification is between 10^{-8} and 10^{-6} seconds. This short solidification time is the result of radial spread of particles, and the increase in surface area of particles after their impact to the substrate. The oxides formed during particle interaction with surrounding medium before impacting substrate would be seen in coating cross section as oxide inclusions (stringers) between lamellae structures formed by splats. [2-3]

The droplet plasticity and velocity must be high enough so the droplets would adhere to substrate after impacting it. Adherence of the coating is usually based on the mechanical bonding, although if the temperature of substrate during spraying is high and the coating environment is inert then chemical bonding is also possible to be achieved. Surface roughening by grit blasting or etching is a primary treatment applied on substrates to increase mechanical bonding.(figure 2 and 3) [2]

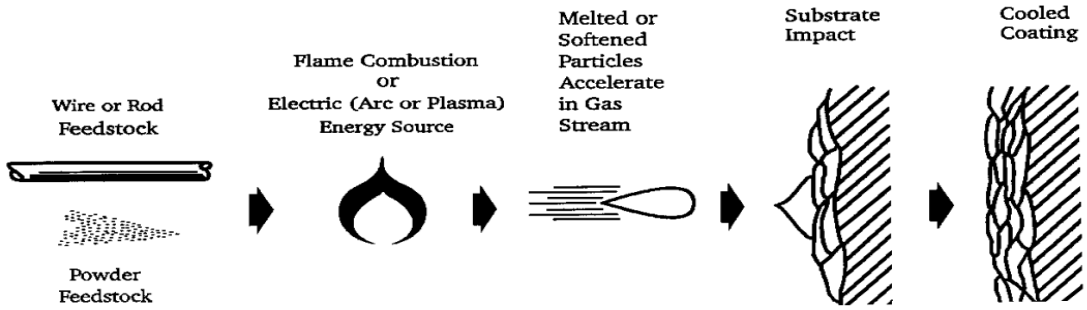


Figure 2: Generic thermal spray schematic. [2]

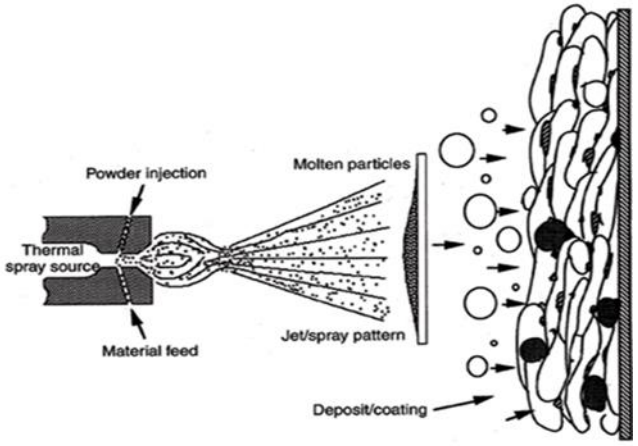


Figure 3: Schematic picture of general thermal spraying process. [4]

Economy of applying and depositing a wide range of coating materials is a really important advantage of thermal spraying coating (TSC). Size of components is not a limit during this process. In most of the thermal spraying methods, the temperature of substrate doesn't exceed 150°C so the properties of substrate material are not altered. Therefore, usually no influence on heat treatments, chemical compositions, etc., occurs. In addition, the tendency of substrate distortion due to substrate heating is so lower than other processes where the substrate is partially molten. Moreover because of low heating of substrate, even easy inflammable materials such as wood, or plastics may be used as substrate material. Low coating/substrate bond strength and coating porosity that can vary from 1 to 20 volume percent are some disadvantages of thermal spraying. Fully dense coatings generally display higher hardness values compared to porous coatings. More over interconnected porosities can be a great concern during thermal spraying of non-sacrificial materials. In addition after deposition of particles onto substrates, the particles start to cool down by the rapid cooling rates (10^4 to 10^6 °C per second). This high amount of cooling rate results in existence of several non-equilibrium phases (amorphous or crystalline) in a single coating. This variation in phases in a single coating results in hardness variation which is not a desirable and beneficial matter. In thermal spraying coating thickness is limited to residual stresses that are formed during coating process, although coatings with 6,35 mm thickness can be produced by this method. [2]

TSC methods that are based on kinetic energy can be divided to two general classifications based on their thermal energy source: Combustion methods and electrical methods. Combustion methods use oxygen/fuel gas flame to generate high enthalpy region and melt the feedstock material. Flame spraying, detonation gun spraying, high velocity oxygen-fuel spraying (HVOF) and high velocity air-fuel spraying (HVAF) are among this branch of thermal spraying. [2]

Electrical methods are higher-temperature coating processes than the combustion methods. Electric wire arc spraying and plasma spraying are among this major branch of thermal spraying. [2]

4.1 Different steps in thermal spraying

Thermal spraying consists of five steps of substrate preparation, generation of the energetic gas flow, particle or wire or rod injection, energetic gas particle or droplet interaction, and coating formation. [3]

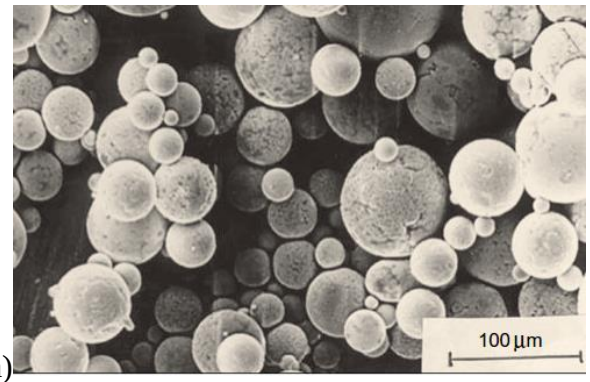
Powder, wire, and rod are generally used as feedstock material for thermal spraying process. Powder manufacturing routes are discussed here duo to the usage of powders as feedstock material during thermal spraying of samples used for experimental part of this thesis work.

The quality of the powder used plays a key role on the properties of obtained coatings. Powder materials have to meet some requirements such as chemical homogeneity, density, flow behavior, size and shape distribution, low cost, etc.

There are various techniques for producing powder materials, the most commons are water and gas atomization, crushing and milling, production by chemical techniques, e.g., solgel, agglomeration, or spray drying, etc. [2] Atomization is applied mainly for manufacturing of metal and alloy powders. Oxides, carbides and cermets powders can be manufactured by sintering or fusion. This process result in blocky and irregular powders, this results in poor flowability of powders. Spheroidization is a process done to improve the flowability of these powders. The spray-drying technique, sometimes called agglomeration, has been applied to manufacture powders of some metals (e.g. molybdenum), oxide and oxide alloys (e.g.Cr_2O_3+TiO_2), nitrides, and cermets (e.g. TiC+Ni or WC+Co). [4]

In fact powder manufacturing route has a significant effect on different powder properties such as size, morphology, microstructure, grain size, and homogeneity of phases and this has a direct effect on obtained coating properties.

(a)



(b)

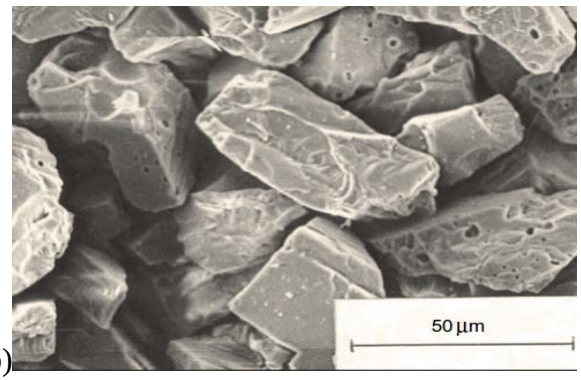


Figure 4: Two types of powder that are manufactured with two different methods of powder manufacturing. The (a) photo: Gas atomization method. The (b) photo: Crushing method. [4]

For example results of other researches show that in WC-Co powder, the WC grain size in cast/crushed powder and the coatings from other produced by them is larger than grain size in powder or coatings resulted powder types. In addition cast /crushed powders display more loss of visible WC during spraying than other powder type, and the sintered/crushed powders seem to be less prone to WC loss during spraying. [3]

Or Seo et al. have showed that coatings sprayed with spherical copper particles showed superior thermal conductivity behavior compared to coatings sprayed with non-spherical particles. This is probably due to irregular morphologies of non-spherical powders which results in higher amount of porosity inside the coating. In another case Streibl et al. has shown that different powder manufacturing routes such as agglomeration and spray drying or crushing and sintering results in different thermal conductivity and specific mass of powders. [3]

4.1.1 Substrate preparation and post-spray treatments

The deposition of powders happens on the surface of the substrate. To obtain an appropriate coating with desired properties, the surface of the substrate should be prepared. All the treatments and processes that are applied on the substrate before coating deposition to make it ready for deposition are called pre-spray treatments. Also some treat-

ments sound necessary to be applied on the as-deposited coating that is deposited on the substrate. For example sometimes as-deposited coating is porous so heat treatment can make the coating denser and less porous. All these treatments that are applied on as-deposited coatings to enhance its properties are called post-spray treatments. In fact it sounds impossible to manufacture good coating on the substrate without applying pre and post spraying processes. This is a fact, even if coating deposition process by thermal spraying is done in an appropriate way. [4] For example the industrial applications of thermally sprayed coatings depends significantly on the bonding strength between the coating and substrate. Surface preparation has a big role to achieve coatings with high bonding strength.

Surface preparation consists two major processes of cleaning the surface, and roughening the surface. Cleaning the surface is applied to eliminate contaminations such as rust, scale, moisture, oil or grease. Solvent rising or vapor degreasing are common ways to clean the surface of material before depositing coating. After cleaning, usually a roughening process of the substrate surface is applied to make substrate ready for coating adhesion. Dry abrasive grit blasting, machining or macro roughening, applying a bond coat are common methods for surface roughening. After cleaning and roughening, the thermal spray coating process should start as soon as possible to prevent oxidation and recontamination of surface. Preheating the substrate before spraying can also be done to release stresses in substrate and drive moisture out from substrate. [2]

Post-spray treatment has a big role in the quality of the coating. Cracks and pores in the coating can be potential places for corrosion and also wear acceleration. These cracks and voids can result in crevice corrosion of coating. In non-sacrificial coatings, Corrosive electrolyte can penetrate to the substrate from these cracks, voids and pores and cause corrosion in substrate. In fact these defects in the coating can make the coating useless. Also pores can result in the initiation of the crack that can propagate and finally cause fracture or wear in the material. By appropriate post-spray techniques one can decrease the amount of the pores and enhance the coating properties. Grinding, polishing, Furnace heat treatment and laser glazing and sealing are classical examples of post-spray treatments. Laser shock processing and spark plasma sintering are two brand new ones. Some of the most common methods would be discussed briefly in the following. [4]

4.1.2 Generation of the energetic gas flow and particle injection

Each specific method has its own way for generation of the energetic gas flow. Cold spraying involves expanding gas, combustion methods depend on combustion or detonation flame, electrical methods depend on plasma and arcs and their interaction with surrounding atmosphere. [3]

Sprayed powders have sizes typically between about 10 µm and 110 µm. Powders are usually characterized by their minimum and maximum diameters: for example 20-40 µm. This means that less than 10 vol. % of the powder is below 20 µm and less than 10% is over 40 µm. Melting of particles depends on different factors such as their morphology, specific mass, size distribution, and trajectories. Powders are introduced into the energetic jet either radially or axially, this depends on the spray gun used. [3]

4.1.3 Energetic gas particle or droplet interaction

This step involves acceleration, heating, melting, oxidation, or changes in surface chemistry of particles (depending on the surrounding atmosphere and particle temperature). This step specifies the trajectory, the impact velocity and temperature for a particle with a specific diameter.[3]

4.1.4 Coating formation

The individual particles strike the substrate and build up the coating. When molten particles impact and strike on the substrate or on top of each other, they show plastic deformation and change into lamella. So after the strike of molten particles on substrate or on each other; they deform plastically and then solidify. Deformation of the particles results in lamellar microstructure which is the characteristic for as-sprayed coatings.

Oxidation is an important and undesirable phenomenon that occurs during coating formation. Deposited lamellas are oxidized during solidification and before the next particle arrival, but this oxidation is not so serious compared to oxidizing during particle flight. Oxidation results in poor adhesion between different lamellas and between lamella and substrate.

4.2 Adhesion of coating

The industrial applications of thermally sprayed coatings depend significantly on the bonding strength between the coating and substrate. Generally, failure of hard coating is not duo to the wear but in fact cohesive failure and failure of the adhesive bond are usual cases of coating failure.

Particles can bond to substrate material by different bonding mechanisms such as mechanical interlocking, adhesion, diffusion, chemical reactions, and sometimes partial fusion. These bonding effects permit the formation of continuous coating layers. Adhesion, diffusion, chemical reactions, and partial fusion are not major bonding mechanisms in thermal spraying process.

Adhesive bonding mechanisms are effective in micro contact areas. Based on the type of atomic bonding, Van der Waals or chemisorption forces can take place in micro con-

tact areas between particles and substrate. Chemical bonds which is the result of valence electrons are the strongest (several eV) and van der Waals (0.1 to 0.4) follows it.

Diffusion and partial fusion are not so major bonding factors since substrate temperature is relatively low and cooling rate of particles during solidification is so high so substrate doesn't melt extensively and would not be diluted by coating material.

Mechanical interlocking is the main mechanism of thermal spray coating adhesion and that is why roughening of the substrate is an important and necessary part of surface preparation. The arriving molten or semi-molten (high plasticity) particles flow around the substrate asperities/roughness, and solidify, this results in establishment of bond between impacting particles and the substrate surface (Figure 5). In fact a kind of interlocking effect occurs between particle and substrate roughness, this interlocking effect is increased by quenching stresses within the spray particles. [2]

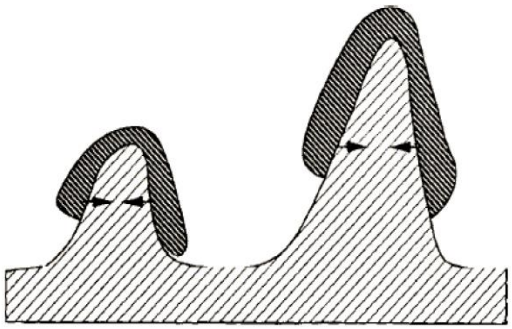


Figure 5: Illustration of mechanical anchorage of splats to irregularities of the substrate surface. [4]

4.3 Stresses within coatings

Residual stresses and service stresses are two types of stress which affect coating. Residual stress is defined as the stress that stay in a body after its manufacturing and is not being subjected to external forces. It can be harmful or detrimental to the performance of coating.

Service stresses can be duo to the thermal effects on coating during service, for example when heating and cooling happens on coating or they can be the result of mechanical stresses submitted on coating during its service life for example when coating is under rolling/sliding contacts. Residual stresses and their origins would be discussed more in the following section duo to its importance on coating behavior.

4.3.1 Residual stresses

Residual stresses that are made and remained in the coating have really high influence and role in the coating property and its mechanical behavior. If there is a stress discontinuity at the coating/substrate interface, for example the coating has overall tensile stress while substrate has compressive stress, this stress discontinuity may result in debonding of the coating or its delamination. Especially during application where tensile stress can even increase. The residual stress also modifies the elastic modulus and hardness of coating, they both increase when the compressive stress is raised. [21]

Quenching stress, expansion mismatch stress, temperature gradient stress, and transformation stress are types of residual stress in coating with thermal origins. Grit blasting, peening effect, grinding and machining can result in another type of residual stress which has mechanical origin.

When fully molten droplets impact on the substrate or the previously deposited layer, they start to solidify. Droplets will start to cool down from temperature TP to the temperature T_{sub} of the underlying material of the substrate or the previously deposited layers. Droplets have this tendency to contract as much as they can but the mechanical anchorage that has happened between the impacting droplet and the substrate or previously deposited layer will hinder the contraction of droplet and it results in a tensile residual stress which is called quenching stress. [3-4]

The theoretical vale of the quenching stress can be calculated by:

$$\delta_q = E_C \cdot \alpha_c \cdot (T_p - T_{sub})$$

Where EC is young's modulus (GPa) and α_c (K^{-1}) the expansion coefficient of the splat. δ_q (MPa) is resulted residual stress.

Coating and substrate have different thermal expansion coefficient (TEC) so as a result when the molten particles impact the substrate and cool down a kind of cooling stress would be generated because of this thermal expansion mismatch. The cooling stress, which can be both compressive or tensile depending on the thermal expansion coefficient of the coating and substrate, is related to coating thickness as formulated by :

$$\delta_{cool}=([E_c(T_f-T_r)(\alpha_c-\alpha_s)])/([1+2(E_cT_c/E_sT_s)])$$

where E_c and E_s are the young's modulus of the coating and substrate. T_f and T_r are the deposition temperature and the room temperature, αc and αs are the thermal expansion coefficients for the coating and the substrate respectively and T_c and T_s are the thickness of coating and substrate respectively. This equation shows that if $\alpha_c < \alpha_s$ then compressive cooling residual stress is obtained which is beneficial, in this case increase of coat-

ing thickness results in lowering of resulted compressive residual stress. If temperature of the substrate is kept constant during spraying, then neither tensile nor compressive cooling stress would be generated. [4]

There would be a high heat flux imposed on the surface of coating during thermal spraying process. There is always a thermal gradient in different depth of coating, especially if thermal conductivity of coating is low. This temperature gradient in coating results in differential expansion in coating and it results in strain misfits in coating. In low thermal conductivity materials , thin coatings should be used to prevent temperature gradient. This kind of residual stress can be inhibited by keeping the surface temperature constant by using cooling devices. [3]

Sometimes after post-spray treatments that happen in the coating or during coating solidification (the exothermic heat of solidification), coating heating causes some phase transformations inside. The new generated phases have more or less different density than the previous one. This change in density causes some stresses in the coating because the coating is attached and cannot deform which are called phase transformation stresses

Grit blasting, peening effect, grinding and machining can result in another type of residual stress which has mechanical origin. During grit blasting compressive residual stresses are generated within a thin layer under the grit-blasted substrate surface.

For spray processes where particle velocities are above 500-600 m/s a shot-peening process occurs. This shot-peening results in a compressive stress which is beneficial. [13-22]

At the end of the coating process the residual stress state whiting the whole coating/substrate system is calculated by considering all residual stresses with different nature that are induced during the spray process. The spray process and processing have key role in stress distribution through the coating and substrate. Using processes with higher velocity results in more effective peening effect and as a result compressive stress in coating. [3]

The stresses produced in the coating can be tensile or compressive and these stresses are produced by different sources and reasons. Based on engineering point of view the overall residual stress which is the combination of tensile and compressive stresses is important and vital to be measured. This overall stress should not be more than the fracture point of the coating material. Generally different materials have more compressive elastic modulus than tensile elastic modulus so in this way compressive stresses in the coatings are more beneficial because the coating can tolerate more compressive stresses than tensile stresses. In addition if a crack is initiated in the coating then compressive stresses would close the crack tip and prevent its propagation, however the tensile stress

would cause its propagation. Moreover, overall compressive stress in the deposited coating lets thicker coating deposition. [4]

4.4 Effect of processing parameters on coating properties

Different thermal spraying processing parameters (temperature, velocity, particle size and morphology, particle grain size, homogeneity of phases in powder, etc.) result in different properties of coating (Adhesion, cohesion, porosity, oxidation, roughness, thickness, residual stress, etc.) and these properties would directly affect mechanical and chemical behavior of coatings. In this section a brief and general description of temperature and velocity and effect of them on obtained properties are discussed.

4.4.1 Temperature and velocity

Particle of powders that are injected to flames or jets are subjected to rapid acceleration and intense heating before becoming in contact with the substrate. The microstructure of the sprayed coating and obtained properties depend strongly to the entire phenomenon that happens for particles during flight time. Particle temperature and velocity are the most important factors and parameters which influence the obtained coating properties. [4]

Jets and flames have very high velocities which accelerate the sprayed particles. The accelerated particles arrive to the substrate and impact with the substrate and form coating. Usually higher particle velocity results in better quality of deposited coating. Dense coatings with stronger adhesion and cohesion can be achieved if the velocity of particles is higher. In addition higher velocities result in higher compressive stress in coating and it means that thicker coatings can be deposited. [4]

Formation of partly molten particles is quite possible during thermal spraying. These partly molten particles contribute considerably to the formation of porosity in sprayed deposits. Porosity decreases the coating hardness. Also porosities in coating can be potential places for crevice corrosion. Interconnection of porosities that result in electrolyte penetration to substrate is a great concern in non-sacrificial coatings. Dense coatings can be obtained if all the particles are melted. However achieving particle with high velocity and all melted is not an easy task. There are two ways for complete melting of the injected particles. Increasing the process temperature or using fine particles. [4]

Increasing process temperature as a solution for complete melting of particles can have some drawbacks. In high temperatures particles may oxidize which is deteriorative for the deposited coating. Oxidation of particles decreases the cohesion between splats by hindering them to bond together during coating formation. Oxides are brittle, so wear

resistance of the coating is decreased and oxidized boundaries between layers can be potential areas for delamination to happen. Also oxidized areas in the coating can accelerate the corrosion. In high temperatures chemical composition of the particles may alter and some materials are prone to be decomposed in high temperatures. Reduction and decarburization are common examples of thermal alteration of particles in high temperatures. In some cases even evaporation may occur in high temperatures. Evaporation can happen selectively and as a result just some elements inside the powder become evaporated. [4]

Another way of achieving complete melted particle is using small particles but small particles are susceptible to evaporation. Vaporization is not desired effect because it decreases the spray efficiency. In addition the vapors may cool down the gas around the sprayed particles and reduce heat transfer. More over the vapors of some materials are not healthy for the operator. [4]

4.5 Thermal spraying methods

TSC methods can be divided to two general classifications based on their thermal energy source: Combustion methods and electrical methods.

Combustion methods use oxygen/fuel gas flame to generate high enthalpy region and melt the feedstock material. Flame spraying, detonation gun spraying, high velocity oxygen-fuel spraying (HVOF) and high velocity air-fuel spraying (HVAF) are among this branch of thermal spraying. [2]

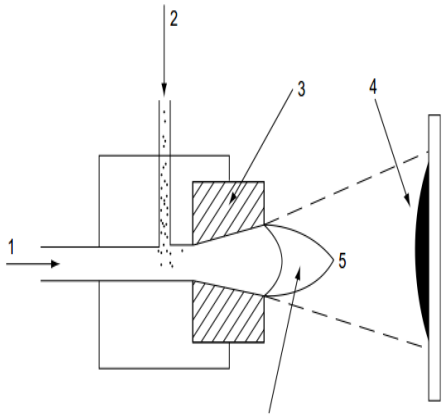
In combustion processes, the highest gas temperature for melting the spray material is got by the adiabatic flame temperature of the combustion gas mixture. This matter reduces the value of these processes for melting high temperature ceramics. Another drawback of these processes is that the environment of the products of combustion process may lead to chemical reactions of the sprayed materials with these gases. [3]

Electrical methods are higher-temperature coating processes than the combustion methods. Electric wire arc spraying and plasma spraying are among this major branch of thermal spraying. [2]

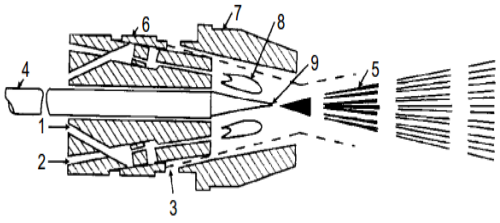
4.5.1 Flame spraying

Flame spraying (Figure 6) is chronologically the first developed spraying technique. In this process the combustion of working gas, which is the mixture of oxygen and fuel, generates high temperature (3000 to 3350K) flame and high pressure stream inside the torch. Powder or wire can be injected to this torch; they would be melted because of the high temperature inside the torch and would be accelerated toward the substrate as a result of the high pressure stream. Powder can be injected axially or perpendicular to the

direction of the working gas. Particle sizes that are usually in the range of 5-100 µm are used during this process. Flame velocity is in the range from 80 to 100 m/s which is so low compared to new thermal spraying methods. The bonding strength between 60-70 MPa can be achieved by this method. [4]



a)



b)

Figure 6: Flame spraying with powder (a), with wire (b). [4]

This process has lower cost compared to other processes. Still, fame spraying is the most widely used process duo to its economics. [3] This process is widely used in industry, i.e., for corrosion resistant coatings. [1]

4.5.2 Detonation gun spraying

This process was the starting point for the development of the flame spraying with high velocity. [2] During this process, the reaction gases (acetylene and oxygen), and a carrier gas for the powdered coating material are inserted into the combustion chamber , mixed and ignited by a spark from spark plug. Release of detonation energy and shock wave created by the combustion of the highly compressed explosive medium, heats the powder and accelerates the powder to the substrate. After each detonation a flushing gas, usually argon or nitrogen, purges the combustion chamber and after that a new cycle starts. There are approximately 4 to 8 detonations per second. Gas velocities of more than 2000 m/s are achieved. The velocity of powder is about 900 m/s when it hits the surface of substrate. High velocity is an advantage of this process. High velocity results in good bonding of particles together and particle to substrate and also dense coatings.

[2] The coatings produced by this method display higher hardness, density and adhesion compared to coatings achieved by flame spraying processes. Wear and corrosion resistant coatings that can operate at elevated temperatures are produced by this process. Also detonation gun spraying is used in applications where close tolerance should be retained, for example in valve components, pump plungers, etc. [1]

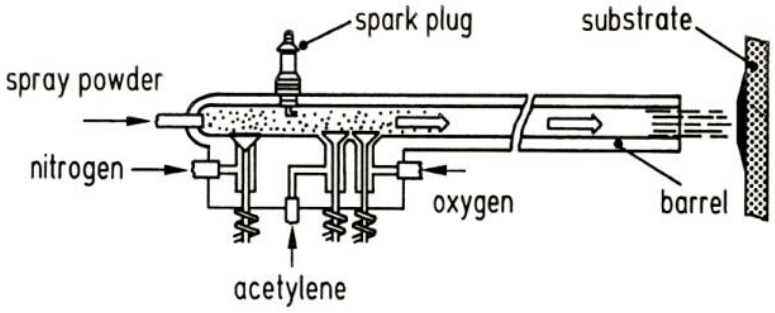


Figure 7: Thermal spray coatings with the detonation gun process. [2]

4.5.3 High Velocity oxy-fuel spraying (HVOF)

The high velocity Oxy-Fuel (HVOF) thermal spray processes are relatively young technologies, the history of industrial application of these processes goes back just whitin the last years. [2]

The working principle of HVOF is somehow similar with D-gun system. The major difference is related to gas burning in these processes. In HVOF the burning is continuous while in detonation gun it is repetitive. [4]

Figure 8 shows the working principle of this system appropriately. As it can be seen, First fuel and oxygen are introduced to the combustion chamber and then this mixture is ignited and as a result combustion happens. The exhausted gas after getting expanded in the nozzle system enters to the barrel from the chamber and this geometry change generates jet. The several different HVOF systems differ with each other in the type of powder injection, the design of the combustion chamber, and the nozzle geometry. Heating and acceleration of the particles occurs in the barrel of the torch, and in the free jet outside. [2]

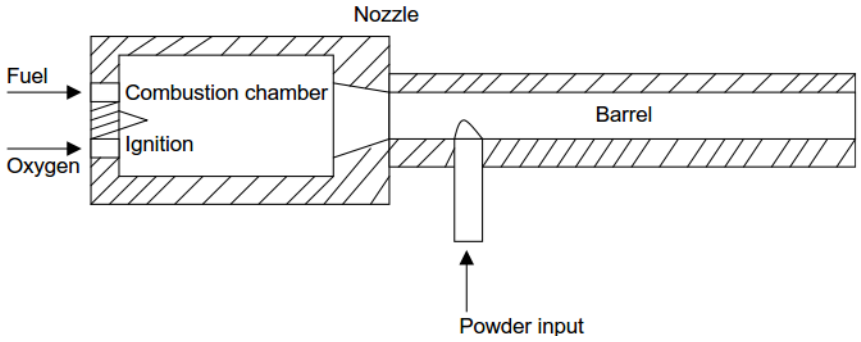


Figure 8: Schematic of an HVOF torch. [4]

The fuel gases used have to be stable under high pressure because the combustion in the HVOF chamber happens in high pressure. Only few types of HVOF systems work with acetylene and this need really high security standards. Lack of acetylene/oxygen usage in most of HVOF chambers result in moderate temperature generation. [2]

The working gas used in HVOF thermal spraying is mixture of oxygen (O2) in the gaseous form and hydrocarbon fuel. Hydrocarbon fuel can be used in liquid (kerosene) or gas state however gas state is more common. Ethylene (C_2H_2), propylene (C_3H_6), propane (C_3H_8) and natural gas are hydrocarbon gases used. [4]

Three general parameters determine the properties of the jet:

(a): Pressure in the combustion chamber: This pressure varies from 0.3-1 MPa to about 4 MPa. Increasing the pressure inside the chamber results in the increase in the velocity of particles. [4]

(b): Profile of the nozzle-barrel: Generally three different profiles are used (i) convergent barrel; (ii) a convergent-divergent nozzle which is called de Laval; (iii) a convergent-divergent barrel. The different profiles result in different pattern in flow of flame and its velocity. [4] When comparing a gun with only a simple straight barrel or with a de Laval nozzle, flow models show that gas velocities were about 300 m/s higher with the de Laval nozzle. [3]

(c):Stoichiometry of the fuel with an oxygen mixture (Based on the combustion reaction). [4]

The following equation shows an example of a stoichiometric reaction. Suppose that propylene is fuel gas.

$C_3H_6 + 9/2\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O + 1936$ KJ/mol

But this equation is just a theoretical chemical reaction, maybe in the HVOF torch the reaction is not under stoichiometry condition. The following reaction defines the variation of working gas mixture in the HVOF torch.

$M=(F/O)/(F/O_{st})$

Values of this ratio should vary from 0.6 to 1.2. But if it is 1, the stoichiometric condition, then the combustion results in the highest temperature that can be obtained. The flame temperature is about 3000°C and high Velocity of about 2000 m/s is achieved that is an advantage for HVOF system. Particle sizes used are generally in the 5-45 µm size range. The powder particles can reach velocities of about 600 m/s. [4]

Typical for HVOF processes are the visible shock diamonds in the free expanding jet, this shows that the Mach number gas glow has been equal or greater than 1. [2] High velocities and relatively moderate temperature are advantages of HVOF processes. High bonding between particles and particles/substrate and also dense coatings obtained are the result of high velocity used in these processes. In addition combination of high velocity and rather low temperature makes these processes appropriate for depositing coating materials that tend to decompose at higher temperatures. In this case, coating materials like WC-Co and Cr_3C_2-NiCr can be deposited without extensive decomposition that occurs at high temperatures. Also HVOF is really efficient in depositing Fe based hard metallic alloys, Hastelloys, Stellites, Tribaloys, and self-fluxing Ni-based alloys. [2] Hardness values of 1100 and 1400± 150 HV5N are obtained for WC/Co deposited by HVOF. In fact the development of HVOF spraying by Browing in 1983 was pushed forward by the need to produce WC-Co cermet coatings with superior properties and without high amount of decomposition.

Abrasion and sliding wear are the main field for HVOF applications. Nozzles of water jet cutting tools, rolls for paper and foil producing industries, sliding areas of pressing irons, valves and pumps in petrochemical applications, and mechanical seals are some examples where HVOF is applied to deposit hard coatings to resist abrasion and adhesion wear. [2] The thickness achieved by HVOF spraying is typically 100-300 µm thick, this thickness allows them to function under extreme conditions. In fact HVOF spraying processes are good candidate for depositing thick cermet coatings for application where sever wear and corrosion are both involved.

As it is already mentioned, some hard cermets are susceptible to decomposition and oxidation in high temperatures of thermal spraying processes. Except in cold spraying which particle surface temperatures are not higher than few hundred degrees Celsius, in other thermal spraying processes particles react with their surrounding atmosphere. Those reactions are mostly controlled by diffusion or convection. Convection occurs in plasma, HVOF, and wire arc spraying under specific working conditions. Convection can increase the reaction rate by up to a factor of 5 compared to just diffusion. Based on

the Arrhenius law, temperature results in increase of reaction kinetics. According to this law, for a temperature increase of 100-200 ˚C, the reaction rate increases by one order of magnitude. As a result, oxidation is very high in for example plasma spraying which the temperature of plasma can be as high as 14000 K and decreases in HVOF with moderate temperature. Oxidation and high-temperature decomposition of the non-oxide ceramic are the main phenomena that occur for cermets containing carbides and nitrides during thermal spraying. For example with WC-Co, the decomposition of tungsten carbide (WC) results in the formation of di-tungsten carbide (W_2C) as well as a high concentration metallic tungsten which is dissolved in the binder phase. When the particle temperature increases, these phenomena occur in more extensive way. These changes in the composition of main particle will affect the coating performance. [3]

Temperature and velocity of particles are two factors which have key role in quality of the coating. A further reduction in particle temperatures below the melting point temperature (To prevent its drawbacks) of metals needs essential increase in velocity, otherwise deposition of coatings with appropriate bonding strength and cohesion is not possible. In fact in the past two decades the trend is focused to extend the process conditions which result in higher particle velocity and lower temperature. [30]

The results of studies show that gas-fuelled HVOF torches produce larger over heating, which results in decomposition of powders, than liquid-fuelled ones. In addition, gas-fuelled torches are somehow more sensitive than liquid-fuelled torches to changes in process parameters and as a result more extensive range of properties can be obtained by gas-fuelled ones.[23] With cermets WC-Co, Cr_3C_2-NiCr rather dense coatings are obtained by using liquid-fuelled HVOF torches [24-29] Further lowering of temperature with substantial increase in velocity is just possible by optimizing the expanding ratio in the diverging nozzle section and by using higher chamber pressure in HVOF processes. To decrease the temperature more and increase the velocity, another thermal spraying method was developed. The High velocity air fuel (HVAF) system was developed to extend the flexibility of high velocity combustion processes. [3]

4.5.4 High Velocity air fuel (HVAF)

The HVAF system was originally developed to reduce the cost of operation and to extend the flexibility of high velocity combustion processes. In HVAF, Pure oxygen was replaced with compressed air to reduce the coast of operation.

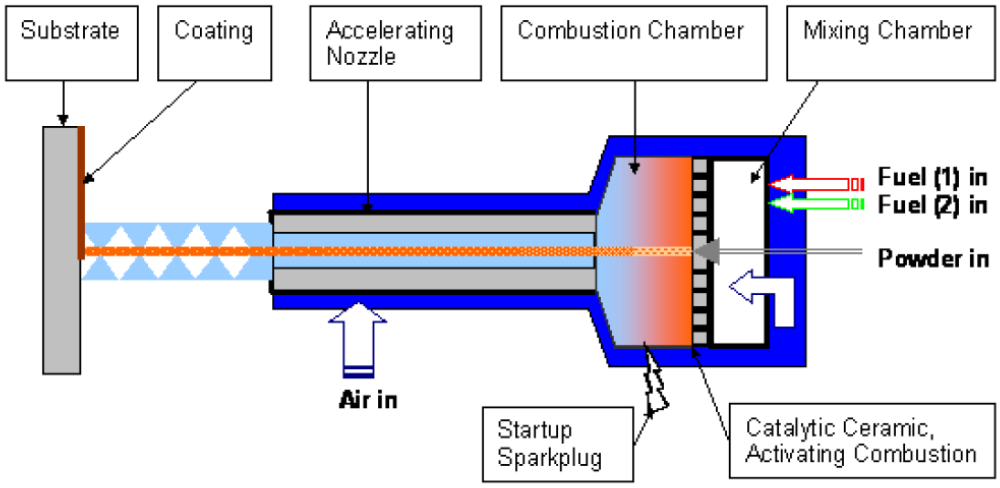


Figure 9: HVAF process schematic.[5]

Compressed air enters the gun as a cooling medium. Then, the air flows into a mixing chamber, where it is mixed with gaseous fuel (propane, propane-butane, propylene). The mixture flows into a combustion chamber through multiple orifices of its catalytic ceramic wall. In the combustion chamber, the mixture is ignited by a spark plug, starting combustion. Within a second, the catalytic ceramic wall is heated above the auto-ignition temperature of the mixture, constantly activating its further ignition and combustion during the whole job cycle. Combusted gases flow into an accelerating nozzle, where their speed reaches sonic velocity. Exhausting gaseous jet has a supersonic speed. [5]

Spray powder is fed axially into the combustion chamber, where it is heated. Then, the powder flows into the accelerating nozzle, where it is accelerated almost to the gas velocity. Leaving the nozzle with exhaust gases, the powder jet is directed to the substrate, forming a coating. [5]

The spray powder's temperature is controlled by combustion process parameters, as well as by small additions of a high-enthalpy and high thermal conductivity secondary fuel, such as hydrogen. Hydrogen (Fuel 2) is fed into the combustion chamber and/or into the powder carrier gas. This approach allows either fusing the spray material or heating it below its melting temperature, whichever is required by the conditions for optimal coating deposition for the specific feedstock material. [5]

In the Activated combustion HVAF Spraying (AC-HVAF) which is the second generation of HVAF spraying processes, spray particles are heated below their melting temperature and particles are accelerated toward the substrate material by the velocity of 700-850 m/s. This process, as it can be seen in the figure 10, is positioned between HVOF processes and Cold spray.

Based on the mechanism of coating formation, coatings can be grouped into two categories. The first category belongs to the coatings formed by mainly fully molten particles which after impacting substrate they flatten and result in splats. The second category belongs to coating which are resulted from the deformation of particles. In this case the particles should be cold and ductile or hot (below their melting temperature) in a plastic state. In addition in this case the velocity of particles should be high enough so the particle deformation can happen after impacting the substrate. In fact in this type of processes the coating results from plastic deformation and peening effect results in its consolidation. HVAF processes belong to the second category so as a result particle velocity has key role in this process. [3]

The following figure demonstrates the trend in lowering the temperature and increasing of velocity in thermal spraying processes. As it can be observed, HVAF has lower particle temperature and higher velocity compared to HVOF.

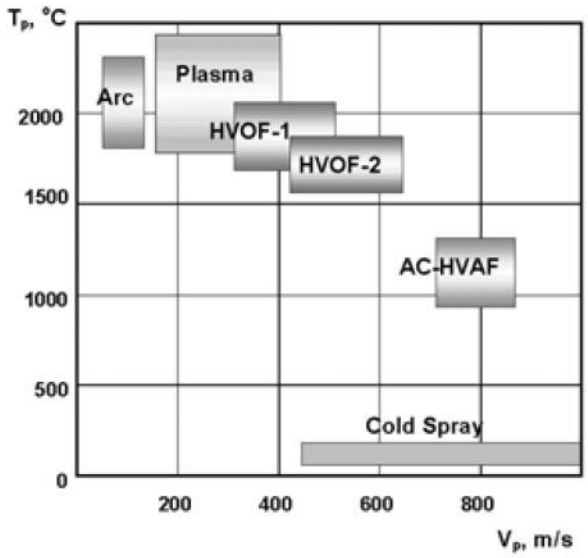


Figure 10: Comparison of spray particle temperature Tp and velocity Vp for thermal spray process. [5]

When the particle temperature reaches its melting temperature, particle melting and evaporation starts. The evaporation rate of particles increase rapidly as the boiling temperature of the material is approached. If melting temperature and boiling temperature of materials are not separated by 300 K, then it will be almost impossible to spray those material with common combustion based processes which particles are melted during the process because the deposition efficiency becomes so low in these conditions. The same issues are considered for decomposition of those materials in high temperatures. HVAF as a combustion base process that particles remain solid can be a solution for mentioned problems. [3]

Relatively lower temperature in AC-HVAF jet avoids material fusion and the particles see little in-fligh oxidation and decomposition compared to other thermal spraying methods because the particles are in solid state and not liquid state. As a result properties of coating such as toughness, hardness, fatigue resistance and corrosion resistance would improve. In addition in AC-HVAF process, particle are accelerated to extremely high velocities toward substrate. higher particle velocities result in more peening effect and as a result more compressive residual stresses in coating which is beneficial and improves coating mechanical behavior and lets thick coatings to be achieved. In addition accelerated solid particles in a spray jet blast away all deposited particles which have poor quality and in this way coating quality is enhanced. [5]

The main applications of HVAF spraying guns are against wear and corrosion. Sliding/adhesive wear, fretting, erosion or cavitation resistant coatings with excellent behavior can be achieved by HVAF process depending on the material and process parameters chosen. [3]

4.5.5 Wire arc spraying

Two wires are used as electrodes in arc spraying. When the electric arc is generated between these two wires as electrodes, they will heat up and melt. So these wires are actually consumed during this process. A gas is used to atomize the molten droplet of the wires. The atomized particles are accelerated toward the substrate under the pressure applied by the atomizing gas. The arc temperature may reach to around 6000K. Arc voltage can change the size of the molten particles. By increasing the voltage the size of the sprayed droplets would increase. Air is usually used as atomizing gas but Nitrogen or the mixture of fuel with oxygen can also be used as working and atomizing gas. Molten particles formed of wires can reach velocities up to 150 m/s.

Figure 11 shows the general mechanism of arc spraying. Number 1 implies the inlet for working gas which atomizes the molten particle of wires, number 5. Arrow number 4 shows the place which electric arc is generated .the accelerated particles are shown by number 3. [4] This process is more economical because of the use of wires instead of powders but this matter makes the materials used in this process limited to ductile and electrically conductive wires. The coatings obtained by this process usually have more porosity than other plasma-based processes. [3]

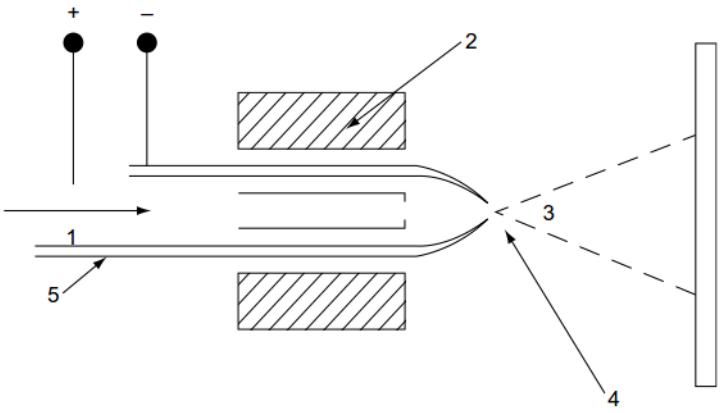


Figure 11: Schematic of an arc spraying installation [4]

4.5.6 Atmospheric plasma spraying (APS)

Plasma can be a good source for heat and stream generation. This can be used efficiently by thermal spraying by using a plasma generator in torch. The electrical discharge between the cathode and anode heats up the working gas. This working gas expands in atmosphere and generates plasma jet stream. When the particles are injected in this jet, they melt and then they accelerate to the substrate. The working gas is usually a mixture of some gases like Ar+He+H_2 or Ar+He+N_2. Each of these gases has a role in the formation of the plasma jet. He, N_2 or H_2 enhance the heat transfer to the particles because they are good heat conductors. Molecular gases usually have higher conductivities compared to atomic ones. The temperature of plasma can be as high as 14000 K. You can see that it is so more than flame spraying temperature. This temperature can melt almost all the refractory metals. The velocity of the plasma jet is also so high, something around 800m/s. Particle sizes are in the range of 20-90 µm . [4] The particle velocities may reach 300 to 700 m/s; this depends on the process design. In addition the high temperature of plasma can melt almost all the materials but it can also result in over fusion and evaporation of some materials. [2]

Atmospheric plasma spraying (APS) is held and applied in surrounding environment which causes oxidation of the molten particles. To avoid the oxidation of molten particles during plasma spraying, Vacuum Plasma Spraying (VPS) is used. VPS gives outstanding properties such as low porosity inside the coating; dense coating with high bonding strength but it is an expensive technique.

If plasma spraying is working in an environment which is not the surrounding environment and also not the vacuum environment and the working atmosphere is somehow controlled then the plasma spraying technique is considered as Controlled-Atmosphere Plasma Spraying (CAPS). [4]

As an example during the spraying of WC/Co by atmospheric plasma spraying (APS), an undesirable eta phase, Co_3W_3C is formed because of carbon losses by air oxidation.

It has been reported that with CAPS, formation of this brittle eta phase can be avoided. [2]

Plasma spraying is commonly used in wear and corrosion resistant applications, i.e., bearing, valve seats, aircraft engines, and mining machinery. [1]

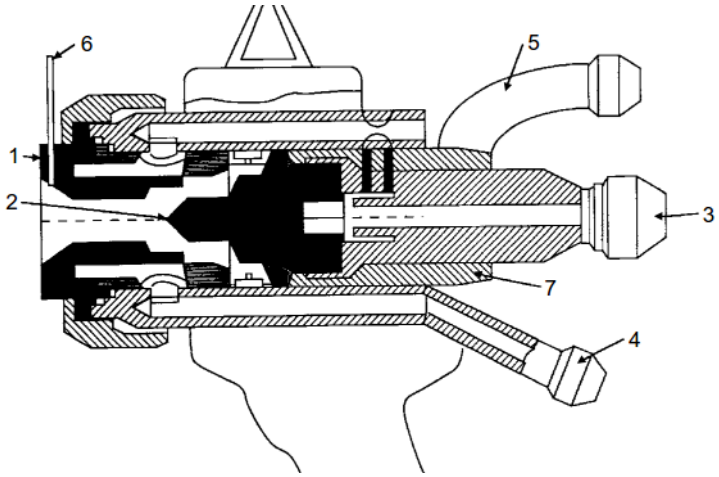


Figure 12:Schematic of a section of plasma torch: (1) anode; (2) cathode; (3)water outlet and cathode connector; (4) water inlet and anode connector; (5) inlet for working gases; (6) powder injector; (7) electrical insulator. [4]

4.5.7 HVOF and HVAF compared to other thermal spraying processes

HVOF and HVAF follow the same kind of process. The main difference between HVOF and HVAF is that HVAF uses compressed air while HVOF used compressed pure oxygen as the combustion-supporting media for the thermal spraying. High velocity air fuel (HVAF) process has lower particle temperature and higher velocity compared to high velocity oxygen fuel (HVOF) process.

Higher velocity and lower temperature is advantage of HVAF and HVOF processes compared to other thermal spraying methods. Higher velocity, above 500-600 m/s results in higher compressive stress duo to the peening effect and lower temperature results in lower amount of oxidation or decomposition of carbides in cermets. Oxidation and decomposition of particles can result in brittleness and ductility diminish and lower fatigue resistant of coating. Oxidation can also result in lower cohesion between splats in coating. [31]

HVAF and HVOF are appropriate thermal spraying process for depositing Cermets such as WC-CO and Cr_3C_2-NiCr. Ceramics with really high hardness are not suggested to be coated by HVAF and HVOF, because ceramics are more prone to high velocities than high temperatures duo to their brittleness. [3] Several researches have been done to understand the behavior of different cermets coated by HVOF and HVAF and the achieved properties of these coatings compared to each other and other coating processes. [32-42]

As it can be observed in figure, HVAF has lower particle temperature and higher velocity (as high as 650 m/s) compared to HVOF. This can be a distinguishable advantage for HVAF compared to HVOF for hindering oxidation and decomposition of cermets, which contain carbides and oxides, during high temperature thermal spraying processes. [43] Based on the Arrhenius law, temperature results in increase of reaction kinetics. According to this law, for a temperature increase of 100-200 ˚C, the reaction rate increases by one order of magnitude. In addition oxidation and decomposition are mostly controlled by diffusion or convection. Convection can increase the reaction rate by up to a factor of 5 compared to just diffusion. Convection occurs in HVOF but not in HVAF because this is in HVOF process that particles become molten and during HVAF process particles mostly remain in their initial state. When comparing the same WC- 12 wt.% Co powder sprayed by HVOF and HVAF processes, results show that amount of W_2C generation and also concentration of W in binder phase was so lower in HVAF processed coating compared to HVOF processed one. [3, 37] In addition lower temperature results in lower tensile quenching stress and higher velocity results in higher compressive stress compared to HVOF deposited coating. It is found that the intensity of the peening action and the resultant compressive stress increase with the kinetic energy of particles. [3] Another processing advantage of AC-HVAF process compared to HVOF is that spray rates are 5-10 times higher in AC-HVAF compared to HVOF.

Several researches have been done about the results of replacement of process from HVOF to HVAF and all show that coatings obtained by HVAF can be so promising due to the different advantages of this method compared to other techniques as it is explained mentioned in the last paragraph. [10, 33, 37, 41]

One of the disadvantages of HVAF compared to HVOF is that coatings produced by HVAF may exhibit more porosity duo to particles not being molten. This issue can be prevented by optimizing processing parameters in HVAF spraying.

5. FACTORS INFLUENCING TRIBOLOGY

Hardness plays an important role in applications where severe wear is involved. In the following section, Mechanisms that result in obtaining a coating with high hardness are introduced. Conventional hard materials and the reason why Iron-based materials can be a possible alternative to solve these issues are discussed.

5.1 Mechanisms influencing the hardness

Achieved hardness in a coating depends on both intrinsic hardness of the used material and also the microstructure of coating.

High cohesive energy (deep potential well), short bond length (large curvature in the bottom of well), and high degree of covalent bonding result in high elastic modulus and intrinsic hardness of material. High bond strength and thus high Peierls (intrinsic lattice resistance to dislocation motion) stress result in a high resistance to dislocation propagation and multiplication and low slip bands. In addition Short bond length implies that material would have high elastic modulus. Also highly directional bonds such as covalent bonds will restrict dislocation propagation. For example in three compounds of TiC, TiN, TiO, and TiC has the highest hardness and TiO has the lowest hardness. This is duo to the higher proportion of covalent bonding in TiC compared to TiN and TiO. In fact by changing the nonmetallic elements from C to N to O, the degree of covalent bonding decreases and the amount of ionic and metallic bonds increase and this means lower amount of bonding strength and directional bonding which can resist against dislocation propagation and multiplication. [3]

Microstructure of coating is another factor that affects hardness of coating. Based on the structure of the coating that is deposited on the surface of the substrate, coatings can be divided to two major types (1) Amorphous coatings (2) Crystalline coatings.

Amorphous coatings which have disordered structure show almost superior properties compared to crystalline coatings, probably because of their higher hardness and lack of structural defects such as grain boundaries and dislocations.

Amorphous structure shows higher hardness than crystalline materials. It can be discussed in this way that the amorphous structure causes dense random packed atomic configuration that resists plastic deformation during the applying of the load and it

means higher hardness. In addition, sometimes in amorphous coating some nanocrystals are dispersed in the coating, these dispersed nanocrystals also contribute to higher hardness of the coatings.

Crystalline structures almost always have some structural defects inside including dislocations, grain boundaries, stacking fault energy and etc. These defects make the crystalline materials susceptible to corrosion. For example grain boundaries have higher energy than the grains so grain boundaries can be potential places for the corrosion start. Amorphous materials don't have these structural defects so they show more corrosion resistance than crystalline ones.

There are some requirements for achieving amorphous coatings. If the cooling rate of the coating is high enough so the temperature of the deposited coating is lower than glass transition temperature then there is probability to achieve amorphous phase. During thermal spraying after deposition of particles onto substrates, the particles start to cool down by the rapid cooling rates (104 to 106 $^{\circ}$C per second). This high amount of cooling rate results in existence of several non-equilibrium phases (amorphous or nanocrystalline) in a single coating. High cooling rate prevents the atomic diffusion and in fact doesn't give enough time to atoms to go to their crystalline lattices and as a result inhibits the crystal formation. In fact in thermal spraying processes the necessary time for solidification is between 10^{-8} and 10^{-6} seconds. This short solidification time is the result of radial spread of particles, and the increase in surface area of particles after their impact to the substrate.

If just high cooling rate is applied then the obtained coating would have crystalline structure with some proportion of amorphous and nanocrystalline phase inside. Some other requirements other than high cooling rate should be applied to ensure achieving a coating with high amount of amorphous content. Glass forming ability of deposited material has the key role to achieve amorphous coating. (1) The alloy system should be multi component (2) There should be large difference between the atomic radiuses of different components in the alloy system. (3) There should be large negative energy of mixing between each two pair of components. This large negative energy of mixing between each two pair of elements causes a short range order in the structure and as a result prevents crystal structure formation. These three requirements mentioned above are called glass forming ability (GFA) of an alloy system .To get amorphous structure from an alloy system after deposition in thermal spraying, that system should have high glass forming ability (GFA) and be cooled in high rates. [44]

If the coating is crystalline then Grain size has a key role in the achieved hardness of coating. Based on the Hall-Petch relation, hardness increases by decreasing the grain size.

$H = H_0 + kd^{-1/2}$

Where H is the coating hardness, H_0 is the intrinsic hardness, and k a material dependent constant.

In fact decreasing grain size means more amount of grain boundary and this results in higher resistance against dislocation motion duo to the pileup of dislocations at grain boundaries. Hall-Petch relation which was originally developed for yield strength is valid for hardness of single-phase coatings with grain sizes as low as 20 nm.

Crystalline structure of the crystalline phase would also affect the behavior of crystalline coating. There are generally three main crystalline structures in metallic materials: Faced center cubic (FCC), Based center cubic (BCC), hexagonal closed packed (HCP). For example FCC materials show more ductility than BCC or HCP materials because of having more sliding planes inside the structure which dislocations can move on them and cause plasticity.

Defects such as voids and pores in coating can affect coating hardness. They can be considered as stress raisers in coating because they can generate tensile stresses. These voids are mostly located in grain boundaries.

High hardness is in fact an advantageous factor for prevention of wear but hardness brings brittleness with itself. It means that after reaching the yield limit, material would not show or just show a little plasticity and cracks would initiate. So the only option for hard brittle materials is accommodating strains within elastic deformation regime, without reaching the yield limit G.Bolelli has discussed that the parameter H/E indicates the ability of material to accommodate strains within elastic deformation regime. So the material with higher H/E ratio is desirable. [45]

As it was discussed in previous chapters, hard cermets are commonly used in applications where corrosion and severe wear are involved. A cermet is a composite material . In this composite, hard ceramics such as borides, carbides, oxides are embedded in tough metal matrix. In fact metal matrix plays the role of the binder of ceramic part and provides plasticity and toughness for the material. Dispersed ceramic would provide hardness and hinders the dislocation movement inside the metal matrix.

5.1.1 Evaluation of tribological properities

Pin on disk sliding test and rubber-wheel dry particle abrasion test are two common tests to evaluate wear behavior of material. Delamination wear, abrasive grooving , adhesive wear and tribo-oxidation are different wear mechanisms that can occur during pin on disk sliding test of thermal sprayed coatings. During rubber-wheel dry particle abrasion test, delamination wear and abrasive grooving are mechanisms that can occur. [46]

Delamination occurs duo to the shear stress produced by the friction force of the pin (in pin-on-disk sliding wear) or repeated impacting of particles (in rubber-wheel dry particle). Cracks would initiate usually in boundary between splats (brittle oxidized areas) as the result of fatigue or resulted plastic strain of these shear forces and then cracks would propagate and delaminate the lamella. [46]

Abrasive grooving takes place by microcutting and/or microploughing. This can occur because of the hard asperities on the surface of the ball (in pin-on-disk sliding wear) moving on coating surface or because of the hard abrasive particles touching the coating surface (in rubber-wheel dry particle). [46]

Adhesive wear is resulted by welding between tiny surface asperities of coating and pin (in pin-on-disk sliding wear). Tribo oxidation may occur during the movement of ball on the surface of coating as the result of generated friction heat. [46]

Mechanical behavior of thermal sprayed coating can be discussed in two levels. Large scale and intralamellar level. Nano hardness test can exhibit intrinsic mechanical strength at intralamellar level and microhardness test can exhibit large scale mechanical strength of coating by considering the effect of splat boundaries and linking strength between them. [46]

Asperities on the pin (pin-on-disk sliding wear) are so small and they would groove just inside the lamella but hard particles that are used in rubber-wheel dry particle test are large enough to affect and groove the coating in large scale. [46] As a result, high nano hardness makes the coating resistant against pin on disk sliding wear. In fact the high nano hardness of coating hinders adhesive wear and abrasive grooving and just delamination of splats may occur extensively as the result of the strain generated by the movement of the pin. In this case, a coating with high nano hardness and high linking strength between splats can exhibit superior wear resistance during pin on disk wear. On the other hand duo to the large scale grooving effect of particles in rubber-wheel dry particle test, this is the microhardness of coating that can be a representative scale for exhibiting the mechanical behavior of coating. Coating with high microhardness would hinder abrasion grooving as the main mechanism of wear in rubber-wheel dry particle test. High micro hardness and good inter splat bonding strength makes coating superior in wear resistance during rubber-wheel dry particle test. [46]

5.2 Conventional hard materials used for resisting severe wear and involved issues

As it is discussed in previous chapters, excellent wear protection can be achieved by HVOF or HVAF sprayed cermet layers. Most common cermets used are WC-based and Cr_3C_2-NiCr. Results show that WC-Co coatings maybe used in temperature ranges up to 550-600 ◦C and Cr_3C_2-NiCr can be use in higher temperatures up to 900◦C. Ni- and

Co-based metal alloys such as Tribaloy, Stellite, Inconel, etc. can also be employed. All these coatings display really good wear resistance and in most of the times corrosion resistance. In fact that is why thermal sprayed coatings of these materials are replaced by electroplated chromium. Chromium plating results in release of carcinogenic Cr^{6+} during the deposition. So these thermal sprayed coatings not only show superior mechanical behavior but also their process has lower health and environmental hazards. But, these coatings still show some serious drawbacks. These drawbacks are related to different reasons. Material safety and health issues, thermal alteration of material during reaction and material cost are the most important ones.

Safety of used material is a major interest of safety regulating bodies around the world. The powders the most probable to be dangerous are those containing high amount of nickel, cobalt, copper and chromium. [3] Specifically these materials such as Ni- and CO-based should not be used at all in food and packaging industry because there is a high risk of product contamination. In fact these powders are potential carcinogens for humans. [46] Results show that WC-Co may result in inhalation toxicity. Exposure to the hard metal dust would cause the so called ‘’ hard metal lung’’ fibrosis. This is duo to some biochemical reactions that occur in body after inhalation of WC-Co and WC-Co-Cr. In fact a compound of WC and Co has more negative effects on health, especially on the lung, than Co or WC alone duo to the contact and increase of corrosion rate of Co as the result of galvanic effect. [47]

In addition as discussed briefly in previous chapter, some cermets are prone to be thermally altered by decomposition and decarburization during high temperature thermal spraying processes. WC duo to its high wettability by most binder metals and also its relative toughness is the most widely used carbide for making cermets. Cobalt is the most commonly used binder of this carbide. WC has no stable molten phase but it is easily transformed to other phases. This makes this material to be difficult in high temperature processes where oxidizing/decarburizing condition is ready. Decarburization, oxidation and dissolution/reaction between WC and metal binder may occur during thermal spraying. These result in the formation of hard and brittle phases such as W2C, Co_3W_3C, Co_6W_6C, Co_2W_4C, $Co_3W_9C_4$, and even WO_3 and tungsten. [3, 48, 49] These hard and brittle phases would significantly affect the toughness of coating. [9]

The last but not the least important issue of these materials is the high and fluctuating prices of Ni- and Co-based alloys and tungsten. This makes coatings manufactured by these materials to be quite expensive. [46]

5.3 Coatings deposited by Fe-based material, the solution

Mentioned issues could be solved by replacing these materials with Fe-based alloys. Thermal sprayed Fe-based coatings have been less investigated compared to WC-Co or Cr_3C_2-NiCr or Ni- and Co-based coatings.

Iron is the fourth abundant element on the earth crust after oxygen, silicon, and aluminum. In fact 4.71 percent of the earth crust mass is Iron. In addition the different extraction processes of iron from iron ore are technologically well understood. These parameters (stable price, different extraction methods, and abundance) and its superior behavior when it is alloyed with other elements make this material really good candidate for different applications.

5.3.1 Hardness mechanisms in Iron-based materials

Hardness of the coating is a key factor in applications where severe wear is involved. If we put different thermal sprayed coating properties such as defects and porosities away and just focus on the material itself then the achieved hardness and wear behavior of iron-based coatings can be based and dependent on different mechanisms and parameters. Grain size, amorphous and crystalline content, different hard phases distributed in iron rich phase are some factors that affect hardness. Solution hardening induced martensitic transformation and strain hardening are other mechanisms that can result in harness increase of iron based phase.

The amorphous nanocrystalline phases are recognized to have an excellent wear resistance, erosion resistance and corrosion resistance. Indeed the chemical and mechanical properties of materials are extensively enhanced when the size of crystallities become nanometric duo to boundary strengthening. Also some amorphous metallic alloys display distinguished mechanical and chemical properties duo to the lack of long range order. [54]

The wear resistance of the coating is related to its microstructure and main phases inside. Hard phases can cause dispersion strengthening. The blocky hard phases (Carbides, borides, oxides,etc.) with the highest volume fraction have very high hardness. Uniform distribution of these hard phases in the ductile and super saturated iron matrix result in good wear behavior. Orientation, size, modulus of elasticity, relative hardness, and brittleness of the second hard phase are factors that affect wear behavior of coating. High volume fraction of hard phase improves the wear resistance of material. But extreme hard phase volume fraction means the lack of matrix and this leads to weak bonding between the matrix and hard phase which results in easy removal of the dispersed hard phase in the wear process. Results show that hard phases such as carbides and borides are frequently formed during solidification of iron based materials. High volume

fraction of hard phase can be obtained by increasing the amount of carbon and other alloy elements which can react with carbon or boron and form carbides and borides during solidification. Some other elements such as B produce significant hardening by formation of interstitial solid solutions or development of hard fine-grained precipitates. [46,59]

solid solution hardening inside iron based phase can occur during solidification of particle. In fact elements such as B, Si, Cr, etc. can solve inside the iron based phase and result in higher hardness by solution hardening mechanism. [46]

Additionally, the induced martensitic transformation, strain hardening and formation of thick protective oxide layers are other mechanisms that if specific conditions are applied can improve wear behavior of coating. [46]

5.3.2 Effect of some elements on the properties of iron-based material

Silicon plays an important role. The appropriate content of silicon is useful to increase the strong glass formation ability. At the same time, it can react with iron and chromium to form silicides with high microhardness. Silicon is the main element in resisting oxidation. Compared with metals, such as iron and chrome, silicon has the advantage to react with oxygen to form SiO_2. Moreover silicon even deoxidizes the metallic oxides. Boron is also more easily oxidized than other metals to form B_2O_3. But SiO_2 shows more excellent flowing power than B_2O_3. SiO_2 lays on the surface of liquid metal, and in this way it can prevent the oxidation of liquid metal. This is the key reason that addition of Si results in low oxidation of thermal sprayed coatings because it separates the molten particles from oxygen by the formation of SiO_2 layer on the particles.

Boron also has strong glass formation ability. Indeed the addition of boron weakens the crystalline structure stability. In fact Boron reinforces the bonds and it leads to increase in bulk modulus. Boron can increase the coating hardness by forming hard phases inside coating and also by solid solution strengthening in Iron-based phase. Boron brings down the melting temperature and this helps in the formation of hard phases. [57]

The presence of chromium in the range of 19-29% besides its partial oxidation during deposition also increases the hardness, the wear resistance and corrosion resistance. Furthermore chromium is also used as grain refiner to decrease the incidence of cracks. [56]

Molybdenum addition to the material with high amount of chromium can be beneficial. The powder with Mo addition has higher anti-corrosion properties. Mo addition results in more stable passivation with wider range. This is because of Mo ability to form

mixed carbides $(Cr,Mo)_{23}C_6$ and this preserves chromium to form a thin layer of protective oxide against corrosion.

Titanium (Ti), Tungsten (W), Vanadium (V) are added into iron-based alloys to form hard carbides and reinforce the metal matrix (TiC: 3200 HV, VC: 2800 HV). In addition formed TiC would result in good thermal stability of coating.

These Fe-based metal alloy coatings that are discussed till now, although being good alternatives for electroplated chromium and other thermal sprayed metal coatings do not show comparable wear resistance with cermets such as WC-Co. Cermet powders with iron-based matrix can be a solution for this issue. Sometime also hard ceramic powders can be blended with Iron-based powder and deposited on coating. [3]

6. COST-EFFECTIVE COATINGS WITH FE AS THE BASIS

Thermally sprayed Fe-based coatings have not been extensively studied and investigated compared to other traditional thermal sprayed coatings. In the following sections the results of some of the researches done about the Fe-based thermal sprayed coatings and achieved properties and their success or failure to substitute traditional hard coatings are discussed. Different Fe-based coating systems and different mechanisms that Fe-based thermal sprayed coatings protect the substrate material and resist against wear and corrosion and also the probable reasons that they are prone to wear and corrosion are discussed in this section.

6.1 Low carbon steel

In some studies that are driven by automotive industry, Fe-based thermal sprayed coatings are evaluated to check if they can appropriately protect the aluminum substrate. Traditionally cast iron is the material used for producing internal combustion engines. These days cast iron is substituted by cast aluminum to reduce weight, which results in fuel consumption and emission reduction. Unfortunately these aluminum alloys that are used for production of engines don't display good tribological properties comparable to cast irons especially in applications involving sliding movement. Deposition of wear resistant thermal sprayed coatings on the cylinder bore wall is one possible way of improving wear resistance of aluminum castings in applications such as lightweight engine blocks. [50,51]

In one investigation the inner surfaces of the cast aluminum engine blocks were coated with HVOF 1020- 2.5% Al type low carbon steel. The coating was produced by a high velocity oxy-fuel thermal spray process from an ASTM 1020 wire stock with 2.5 wt. % Al addition. [50]

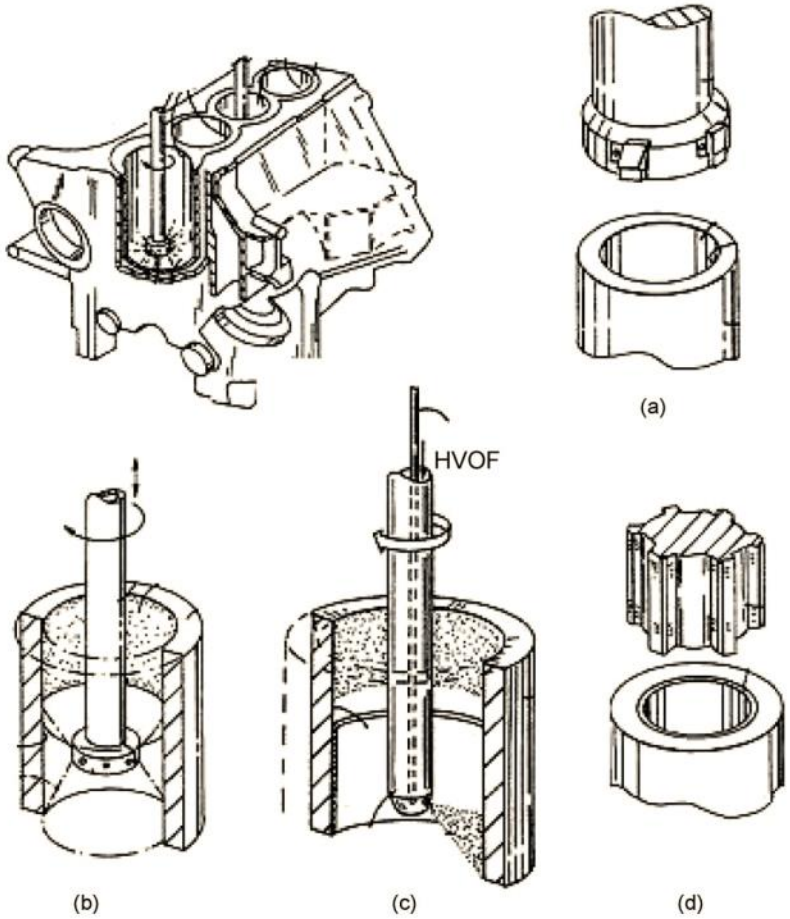


Figure 13: Schematic of the thermal spray deposition process inside a cylindrical sample: (a) the boring of the cast cylinder wall; (b) the water jet cleaning/surface roughening treatment of the cylinder wall; (c) the application of the thermal spray coating to the cylinder wall; (d) the honing of the cylinder wall to the finished dimension. [50]

The coated engine was installed in a prototype vehicle to evaluate and analyze the wear mechanisms that occur in thermal sprayed coating. It should be mentioned that this iron-base coating is a typical example of iron-based coating without any dispersed hard phase. Results show that splat delamination was the main wear mechanism. The microstructural investigation shows that FeO and $FeAlO_3$ oxides are generated between the splats and actually these oxides are the potential places for crack initiation and propagation during sliding movement in cylinder. Figure 14 shows that cracks propagated along the oxide veins at the Fe/FeO interfaces or Fe/$FeAlO_3$ which have low fracture toughness. These results suggest that reduction of oxide between the splats may lead to an improvement in wear resistance of these coatings. [50]

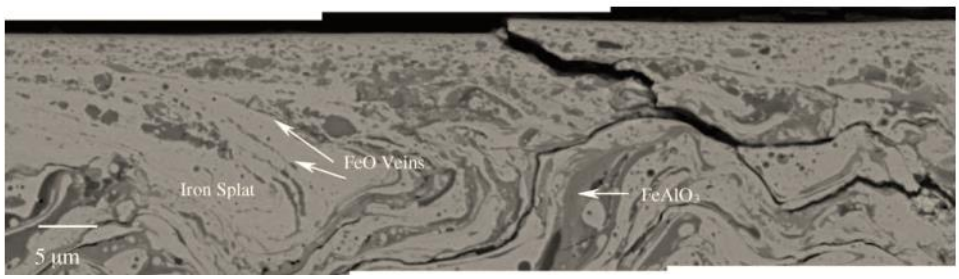


Figure 14: Oxide stripes formed between the splats of Iron-based thermal sprayed coatings.[50]

Edrisy et al. has done more researches on these coatings to obtain more information about wear mechanism of these conventional Iron-based coatings deposited on aluminum cast components. Conventional low carbon steel (0.2% C) was deposited on 319 Al alloy substrates by a plasma transfer wire arc (PTWA) and then these coatings were subjected to dry sliding tests over a range of loads (5-75) and sliding speed (0.2-2.5 m/s). The obtained coating shows the low hardness of 310±10 kg/mm^2 hardness and the microstructure of thermal sprayed steel coatings consist of iron splats that are separated by thin oxide layers of FeO. These investigations were done to acquire the wear rate and mechanism of these coating in different sliding load and velocity.

Sliding test was the best test to evaluate the behavior of these coatings in practical applications because these iron based coatings are used to protect inner surfaces of the cast aluminum engine blocks during the sliding of piston in the cylinder. The result show that different wear rates and mechanisms can happen based on different sliding load and velocity. In fact based on wear rate and mechanism, the behavior of coating can be divided to four regimes. Regime I occurs at low sliding loads i.e., below approximately 1m/s and 20 N. Regime II occurs at loads above 20 N and sliding velocities lower than 1 m/s. Regime III exists at sliding velocities above those in regime II, and the same load levels. Regime IV occurs at sliding velocities above 1 m/s and loads approximately below 20 N. [51, 52]

Oxidation of iron splats or formation of Fe_2O_3 is the main reason of wear in regime I. These oxides are loose and during sliding they would detach from surface. Sever deformation of the steel splat tip and splat fracture and fragmentation is the character of wear in regime II. This regime showed the highest wear rate and this is duo to the formation and propagation of subsurface cracks whit in the oxide veins. Oxide veins cause weak links with low toughness between the splats that could be potential areas for crack propagation during sliding. Thick protective oxide is formed in regime III. In fact after a critical velocity in sliding, the wear rate starts to decrease and the wear mood changes from severe wear to mild wear. Frictional heat is generated duo to the high velocity and it can have two effects on coating. Generated heat can result in thick oxide layer formation which protects the coating from more wear and reduces the friction or this heat can attribute in self-induced quench hardening process in iron splats and hardening of

the coating. Formation of mixed oxide layer and no evidence for the splat tip fracture is the main reason of wear at regime IV. [51,52]

As it is mentioned the highest amount of wear occurred in regime II duo to splat delamination. Oxidized regions have been the areas that crack have initiated in them and finally delamination has happened. These results suggest that reduction of oxide between the splats may lead to an improvement in wear resistance of these coatings.

6.2 Stainless steel

Stainless steel is another conventional Iron-based material which can be thermal sprayed on substrate to protect it against wear and corrosion. Stainless steel does not show high hardness and its application is mainly for corrosion prevention. Porosity and oxidation exist in almost every thermal sprayed coating. These can affect the corrosion behavior of thermal sprayed stainless steel. Interconnected porosities can result in penetration of liquid to substrate and make stainless steel coating useless if it is nobler than substrate. In addition porosities and inhomogeneities on the surface of coating can make it prone to crevice corrosion. Oxidation results in depletion of Cr near the boundaries of oxidized splats and it can cause corrosion.

Stainless steel 316 (AISI 316L) coatings were sprayed on carbon steel substrate by two different methods of HVOF and HVAF and different particle sizes. HVOF resulted in denser coating with less porosity compared to HVAF one but more oxidation as it is expected. Furthermore smaller particles resulted in higher amount of oxidation in coating but less amount of porosity compared to larger particles in both spraying methods. In addition coatings were sealed to see how much sealing process can be effective in decreasing corrosion.

The results show that when unsealed coatings are used, HVAF coatings show higher corrosion compared to HVOF ones. This is because of existence of interconnected pores that result in penetration of corrosive electrolyte and corrosion of substrates and also crevice corrosion that happens as the result of corrosive medium penetration to these pores. Corrosion is more if larger particles are used for spraying HVAF coatings. Because using larger particles result in higher amount of porosity.

When coatings were sealed, corrosion was less on the HVAF coatings than corrosion on the HVOF coatings. In fact sealing closes the interconnected pores that exist in HVAF coatings and doesn’t let the corrosive electrolyte to pass coating and reach substrate or result in crevice corrosion. The only way that corrosion happens is around oxidized areas that Cr is depleted. So HVOF sprayed coatings show higher corrosion because of having more oxidized areas and as a result more Cr depleted zones which result in inferior corrosion behavior. In fact sealed HVAF coatings which are deposited by larger

particles do not show any significant corrosion and this is because of lack of particle oxidation during process. [53]

As Zheng et al. explains, these results show that while the amount of pores dominate the corrosion resistance of as-sprayed stainless steel coatings, the degree of oxidation of the coatings determines the corrosion resistance when sealing is applied. [53]

These results suggest that oxidation and porosity should be diminished to have a coating with superior corrosion behavior and if reducing oxidation is with the coast of having higher porosity in the coating then sealing is a necessary treatment.

6.3 FeCr/Ni system

In recent years, FeCr alloys have received attention as high-temperature oxidation and wear resistance materials for the requirement of the utilities to enhance the thermal efficiency of fossil fired power generation plants. A number of high strength 9-12% Cr steels have been applied as construction materials in such advanced power plants. FeCrNi and FeCrAl thermal sprayed coatings have already been successfully used in the applications where corrosion, wear and oxidation resistance at elevated temperatures are involved. Chromium can oxidize and result in protective oxide layer which hinders more corrosion and in addition chromium addition to Fe material causes secondary hardening when its content is more than 10% and decreases stacking fault energy of austenite, both of these factors lead to increase of the wear resistance. [65]

In a study, FeCr/Ni-based coatings were produced on plain carbon steel substrates by thermal spray method to be evaluated for several applications in power generation plants. Plain carbon steel substrates were coated with a bond layer using Ni-based powders and then FeCr (Fe=87.60 and Cr=12.40) powders were sprayed on this bond layer. In fact Ni-based bond layer is used between the substrate and FeCr coating to increase the adhesive strength. In addition, Ni,Cr and Ti used in Ni-based bond layer propmote resistance to oxidation and high temperature corrosion and promote the hardness of the coating by forming very hard precipitates. [65]

Table 1: Composition of Ni-based powder. [65]

Composition of Ni-based powder

Composition	Ni	Cr	Al	Mo	Si	B	Fe	Ti
Weight percentage (wt.%)	73.5	8.5	7	5	2	2	1	1

XRD results indicate the formation of FeCr, Fe, Cr and Fe-Cr-Ni phases in the coating. Also some oxide including Fe_2O_3 and Fe_3O_4 are observed by XRD. [65]

Microhardness of coating was measured as a function of distance from the surface of top coating (Fig 15).

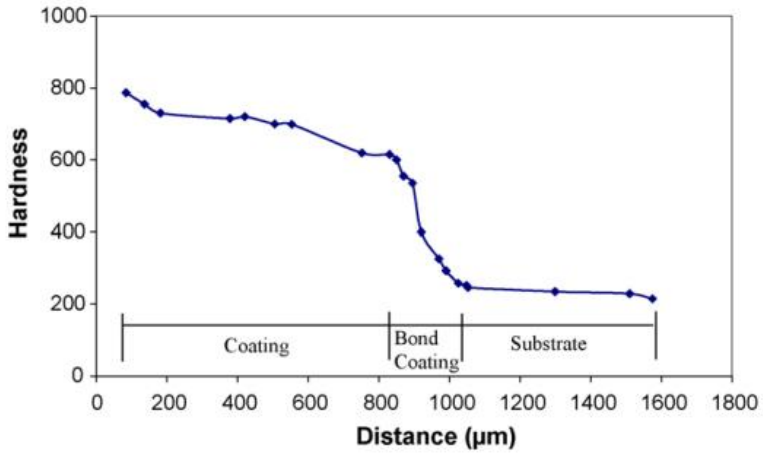


Figure 15:Microhardness (HV) values of FeCr top and Ni-based bond coatings and the substrates as a finction of distance from the surface of top coating. [65]

FeCr coatings were subjected to sliding wear against AISI 303 stainless steel counter bodies under dry and acidic environment. A pin-on-plate type apparatus was used with normal loads of 49 and 101 N and sliding speed of 1 Hz. Wear loss results can be seen from the following figure. [65]

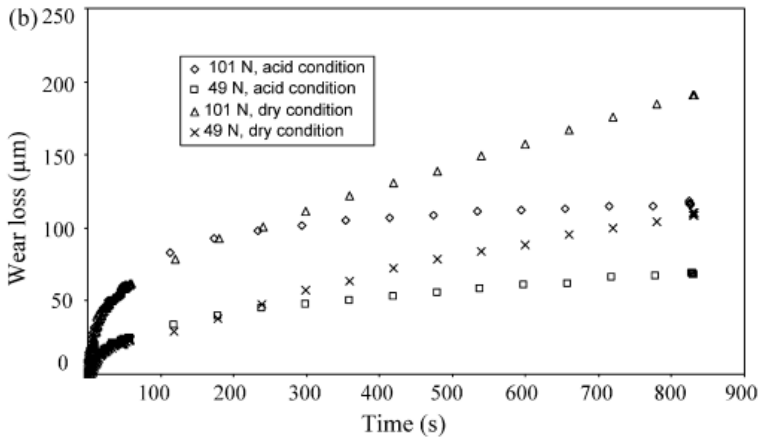


Figure 16: The variation of wear loss of FeCr coating as a function of sliding time for 49 and 101 N loads .[65]

As it can be seen, in acidic conditions, a steady state condition occurs by passing time, while in dry environments wear loss of the coating shows increasing trend by passing time.

6.4 FeCr, FeCoCr, FeCoCrNi and FeCrNi systems

In another study five iron based coatings with different compositions of FeCr, FeCoCr, FeCoCrNi and FeCrNi were deposited by electric arc thermal spraying on carbon steel to increase its corrosion resistance. Five chemical compositions were tested in order to give a large panel of variation and possibility.

The following table presents the chemical composition of wires used in thermal spraying.

Table 2: Chemical composition (wt %) of wires used in electric arc process. [56]

Chemical composition (wt%) of wires used in electric arc process.

Wire	Fe	Co	Cr	Ni	B	Mn	W	Mo	C	Si	Cu	P	N	Nb
A	66.1		27.0		3.5	1.8				1.6				
B	65.7		25.7	2.9		1.9		0.8	1.6	1.4				
C	3.6	58.4	28.8	1.9		0.9	4.9	0.02	1.1	0.3				
D	68.5		19.6	9.1		1.5		0.5	0.02	0.3	0.4	0.03	0.07	0.01

and this table shows the combination of wires used to obtain coatings with different compositions.

Table 3: Combination of wires. [56]

Condition	Combination of wires	Intermediate bond
1 (FeCr)	A + B	95Ni5Al
2 (FeCoCr)	A + C	95Ni5Al
3 (FeCoCr)	B + C	95Ni5Al
4 (FeCoCrNi)	C + D	78.3Ni20Cr1.4Si0.3Fe
5 (FeCrNi)	D + B	78.3Ni20Cr1.4Si0.3Fe

The following figure presents the average hardness of each coating with specific composition.

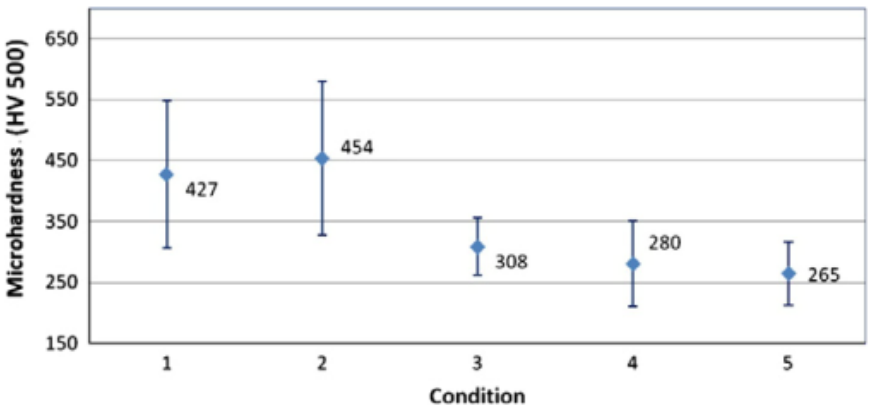


Figure 17: Average microhardnness (HV 500hg) of coatings. [56]

The presence of chromium in the range of 19-29% in coatings can cause the formation of carbides and increase the hardness of coatings. In addition chromium and increase the corrosion resistance by forming protective layer of oxide in coatings. The higher hardness of conditions 1 and 2 could be related to the possible formation of borides along carbide duo to the existence of boron in wires used for spraying them. [56]

This moderate amount of achieved hardness makes these coatings interesting for applications which involve typical wear (not severe).

To evaluate the corrosion resistance of these coatings, sealed (epoxy) and unsealed samples were tested in salt spray chamber for 36 h at 35 ˚C in chloride medium.

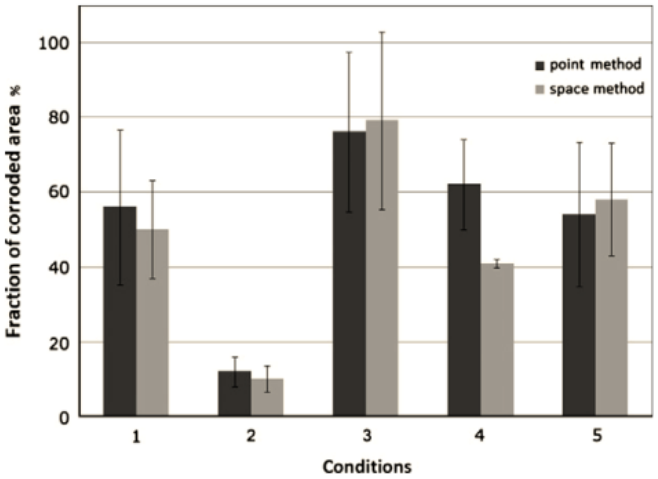


Figure 18: Fraction of attacked areas after salt spray exposure for samples without sealing. [56]

As it can be observed from Fig 19, unsealed samples showed intense corrosion. The samples with epoxy sealant are attacked at negligible intensity.

In addition complementary electrochemical tests display that sealed samples have a global corrosion potential of at least 150 mv nobler than non-sealed ones.

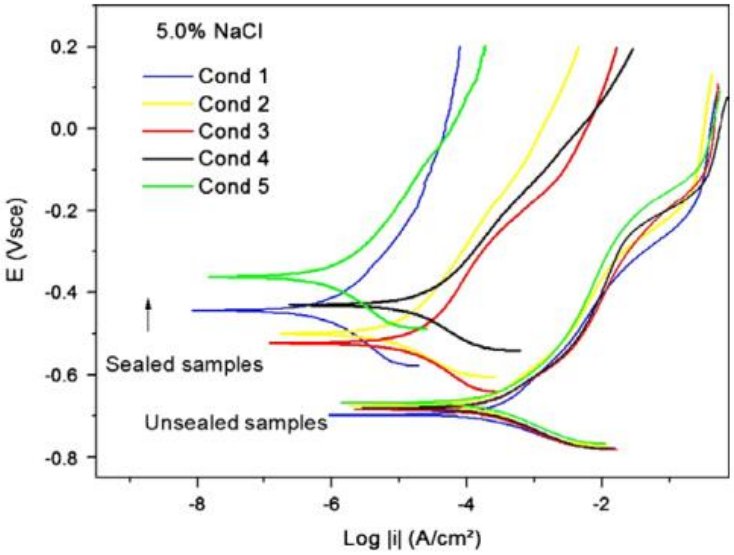


Figure 19: Potentiodynamic polarization curves of sealed and unsealed samples. [56]

Samples without epoxy displayed intense corrosion and the visual results were capable to detect different behaviors. As figure 19 exhibits, the corrosion current densities of unsealed samples were very higher than those of epoxy-sealed surfaces at same potential.

These results suggest that sealing and bond coating has a prominent role to protect coatings from corrosion of aggressive environments. In fact intense corrosion occurs in coatings without sealing or bond coating so they are not reliable in aggressive marine conditions.

6.5 Fe25Cr3B2Si (Armacor M), Fe27Cr5C and Fe39Cr5C System

Three iron-based coatings: Fe25Cr3B2Si (Armacor M), Fe27Cr5C and Fe39Cr5C were deposited on a mild steel by three arc-spray processes. The following table shows the three different processes used and some obtained properties.

Table 4: Iron-base coatings. [55]

Target iron-base coatings

Coating	Nominal composition	Wire type	Spray process	Hardness (HV)	Porosity (%)	Oxide (%)
Standard Armacor M	Fe27Cr3.5B3Si	Cored wire	Standard arc	723–803	4–6	4–7
CA Armacor M	Fe27Cr3.5B3Si	Cored wire	Combustion arc	590–650	<1	5–8
HVCC Armacor M	Fe27Cr3.5B3Si	Cored wire	HVCC	606.7	<1	3–4
Standard Fe27Cr5C	Fe27Cr5C	Cored wire	Standard arc	348–557	4	5–7
CA Fe27Cr5C (DS-100)	Fe27Cr5C	Cored wire	Combustion arc	541	<2	6–8
HVCC Fe27Cr5C (UTEx 5-334)	Fe27Cr5C	Cored wire	HVCC	561	<2	6–8
Standard Fe39Cr5C	Fe39Cr5C	Cored wire	Standard arc	444–554	3–4	5–7
CA Fe39Cr5C (DS-110)	Fe39Cr5C	Cored wire	Combustion arc	447–494	<3	6–8
HVCC Fe39Cr5C (UTEx 5-335)	Fe39Cr5C	Cored wire	HVCC	543	<2	6–8

As it can be observed Fe25Cr3B2Si (Armacor M) displays higher hardness compared to two other materials and this is duo to the effect of boron inside the composition of this material which results in formation of hard phase in coating.

The elevated temperature erosion behavior of these three iron-based coatings sprayed with three different methods are compared together. The results are shown in the following table.

The results clearly shows that microhardness is not a sole factor affecting on the erosion resistance of coating and the structure of coating obtained by different processing methods is a more important factor. As it can be observed in table, the coatings sprayed with HVCC process were slightly better than other ones. This is mainly duo to the denser structure with less porosity coatings which are obtained by this process.

In addition by raising the impact angle from 30 to 90◦ , the thickness loss of three iron-based coatings increased drastically. This shows a strong brittle behavior erosion behavior of these coatings especially for Fe39Cr5C. Material loss mainly occurred by chipping and loosening of cracked surface plates, initiating at the splat boundry, porosity and oxide interfaces. [55]

Table 5: Erosion thickness loss of target materials (µm). [55]

Erosion thickness loss of target materials (µm)

Target material	Bed ash A (at 30°)	Bed ash B (at 30°)	Bed ash B (at 90°)
1018 Steel	391	59	42
Standard Armacor M	89, 112	24, 30	82, 88
CA Armacor M	88, 119	26, 30	72, 69
HVCC Armacor M	76, 79	21, 28	65, 62
Standard Fe27Cr5C	99, 109	29, 34	119
CA Fe27Cr5C	97, 103	27, 25	93, 102
HVCC Fe27Cr5C	79, 89	18, 16	85, 89
Standard Fe39Cr5C	92, 99	45, 48	Worn through
CA Fe39Cr5C	91, 105	40, 41	261, 289
HVCC Fe39Cr5C	74, 82	19, 26	136, 135

The results of this research shows that coating hardness is not a sole factor affecting on the erosion resistance of coating and the structure of coating obtained by different processing methods is a more important factor.

6.6 Fe-Cr-B system

Fe-Cr-B- based alloy coatings (Armacor) with two different compositions were weld-surfaced by the plasma transferred arc (PTA) process. The composition of two Fe-based gas atomized powders used are presented in the following table.

Table 6: Composition of used powders. [58]

	Armacor C	Armacor M
Composition (wt.%)	Fe: balance Cr: 30–32 Ni: 17–19 Mo: 3.5–4.5 B: 3.5–4.5 Cu: 2.2–2.8 Si: 1.0–1.8 Co: 8.8–11	Fe: balance Cr: 44.5 B: 5.9 Si: 2 S: 0.2 maximum

The structure of both coatings consists of hard-phase precipitates of borides in softer iron-based matrix. The XRD pattern indicates that Cr_2B and $Cr_{1.65}Fe_{0.35}B_{0.96}$ are the formed borides in coatings. XRD results didn't show presence of any significant amount of amorphous phase. Armacor M coating shows higher hardness(814 HV) and larger boride hard particles compared to Armacor C (508 HV) coating and this is because of the existence of more amount of Boron and Chromium in powder. Boron and chromium can react with each other and form hard boride particles in coating. [58]

Pin on disk sliding test and three body abrasive tests were done on both coatings to evaluate their wear resistance. Results show that Armacor M coating with higher hardness and larger boride particles exhibits better wear performance than Armacor C coating for all wear testings. [58]

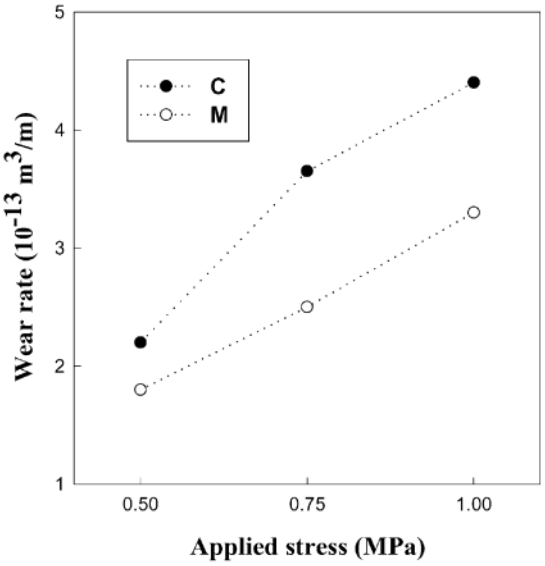


Figure 20: The effect of applied stress on the wear rate of the pin for the pin-on-disk sliding wear test (sliding speed: 0.8 m/s; total sliding distance: 9048 m) [58]

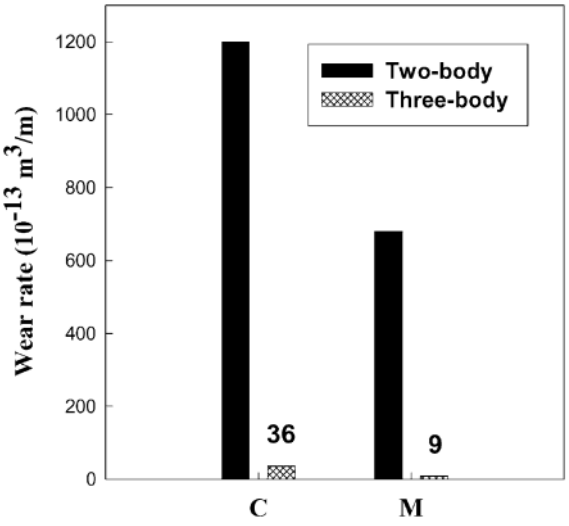


Figure 21: The results of abrasive wear testing [58]

Delamination wear mechanism was the main wear mechanism observed in these coatings. Delamination happened after propagation of the cracks around the splats or oxide stringers. [58]

6.7 Fe-Cr-B-Si self-fluxing alloy system

A commercially available Fe-Cr-B-Si self-fluxing alloy powder with the nominal composition Cr-13.6, B-1.6, Si-1.1, C-0.16, Fe-balance (wt.%) was deposited by supersonic

plasma spraying process. Based on the XRD results α-Fe/Cr is the main phase in the coating. In addition metallic carbides such as FeC_3, Cr_7C_3 are also in the coating. More detailed information of the microstructure of the coating was given by HRTEM. It reveals that the main phase in this Fe-based coating is α-Fe and amorphous phase. Obtained amorphous phase is the result of appropriate processing parameters and also existence of Si and B in the composition of powder. Furthermore the dimensions of the α-Fe crystal grains range from 200 to 700 nm. The amorphous nanocrystalline phases are recognized to have an excellent wear resistance, erosion resistance and corrosion resistance. Results show that the coating hardness is greatly increased because of the dispersion strengthening of these hard phases and also formation of amorphous phase and grain boundary strengthening of nano size grains. [54]

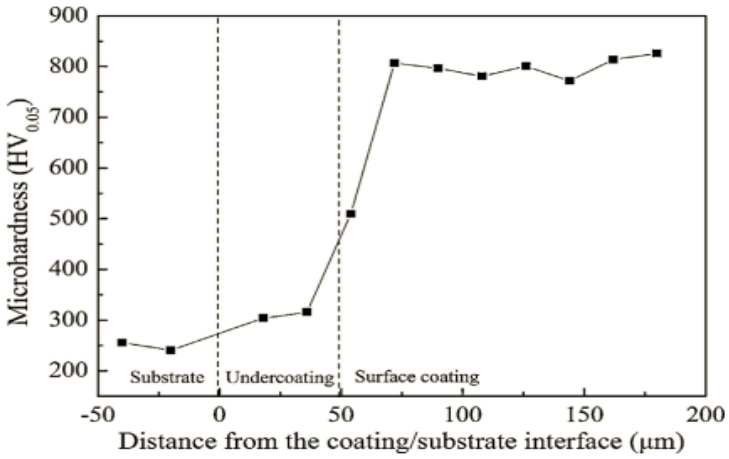


Figure 22: Distribution of microhardness within coating/substrate configuration. [54]

Low oxide coating was obtained duo to the self-fluxing effects of Si and B.

In another study, commercially available Fe-based alloy powder was used as the HVOF-sprayed raw material. The powder composition was 44.7 wt.% Cr-5.8 wt.% B-1.98 wt.% Si, balance Fe, with negligible amounts of C, Mn and S. The powder was coated on substrate of stainless steel plates by HVOF. XRD results reveal the existence of some boride phase in the powder along the iron-rich phase.

During the HVOF thermal spraying the temperature of flame flow is around 3000 ˚C and in addition the in-flight particle speed is so high. This resulted in incomplete melting and dissolution of boride phase in powder. However this even incomplete melting of boride has two effects. One is that the boron resulted from melting of boride would be beneficial for solid solution strengthening of iron rich phase solution and amorphous phase formation. The other is that the many randomly distributed un-melted borides will cause dispersion strengthening and hardness would be increased. In fact, the combination of un-molten well distributed borides that result in dispersion strengthening, amorphous phase and solid solution strengthening that has occurred in Iron rich phase (

from dissolution of B, Si, Cr, etc. in Iron) result in a coating with high hardness. In addition the crystalline part of the structure had really small grain size (nano size) and this also contributed to achieve high hardness in coating by grain boundary strengthening effect. [63]

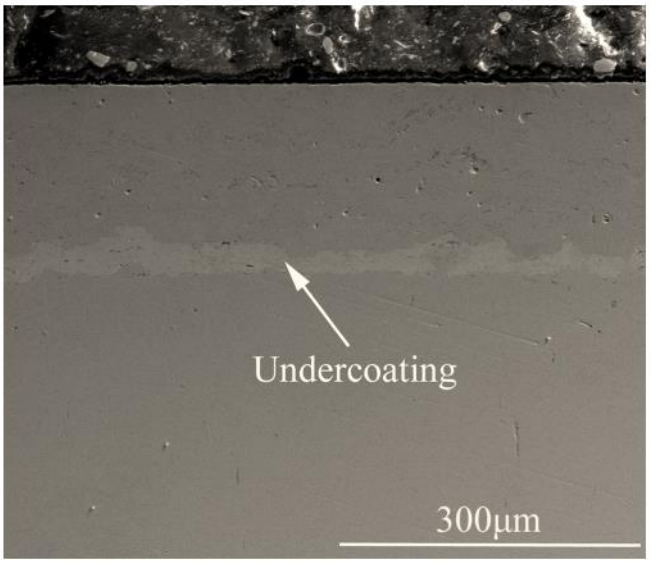


Figure 23: Cross section of the deposited coating. [54]

Measured Hardness across the coating and substrate is represented in the following figure.

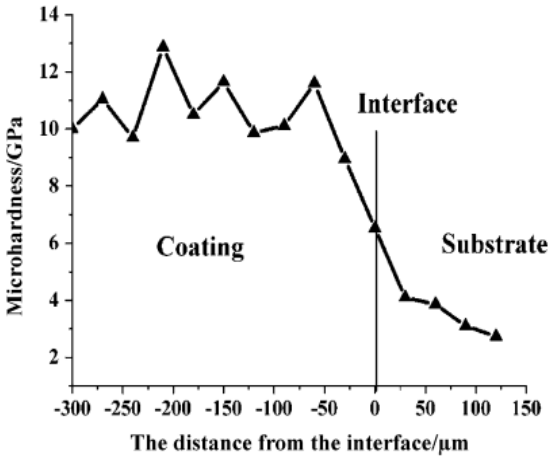


Figure 24: Hardness across the coating and substrate. [63]

The results of these studies suggest that reducing the grain size (boundary strengthening), obtaining amorphous phase, and solid solution strengthening can result in high hardness and good mechanical behavior in coating.

6.8 High chromium iron base hardfacing alloys

The high chromium iron base hardfacing alloy is used in a wide range of industries to extend the life of machine components which are specifically subjected to abrasive wear. [59] Eutectic, hypoeutectic, and hypereutectic are the structures that can be obtained based on the composition of high chromium iron base alloys. Eutectic alloy consists of iron matrix (i.e., austenite, martensite, ferrite, pearlite, or bainite) and carbide, hypoeutectic alloy consists of proeutectic austenite phase and eutectic phase , and hypereutectic alloy consists of proeutectic carbide phase that is embedded in eutectic phase.

The hypereutectic alloys are considered as the preferred hardfacing alloy for applications where harsh abrasive working conditions are involved. Because as it is discussed they have more hard M_7C_3 carbides (proeutectic carbides and carbides in eutectic phase). In M_7C_3, M includes Fe, Cr and other carbide forming elements. The amount of carbide volume fraction (CVF), can be increased by increasing the amount of carbon(after eutectic point) and other alloy elements such as Ti and V that can react with carbon and form carbides(TiC :3200 HV, VC :2800 HV) in these high Cr hardfacing alloys. In fact the wear resistance of these materials results from factors such as the hardness, the carbide volume fraction (CVF), size and distribution of them. High volume fraction of carbides improves the wear resistance of material. But extreme hard phase volume fraction means the lack of matrix and this leads to weak bonding between the matrix and carbide which results in easy removal of the dispersed hard phase in the wear process. These hypereutectic high chromium hardfacing alloys can also be used for repairing the damaged components that are required to endure harsh abrasive conditions. [59]

The effect of boron on microstructure and wear properties of hardfacing alloys was investigated. A new type of Fe-Cr-Ti-C self-shield metal cored wires with varying amount of boron (0 wt. % B, 0.35 wt.% B, 0.67 wt.% B, 0.99 wt.% B, 1.40 wt.% B) were deposited by arc welding. Results show that the CVF of five samples are 14.10, 18.67, 23.99, 29.87 and 36.00%, respectively. As the result clearly show, CVF increased by increasing boron content.[59]

The following figure shows the effect of boron on the hardness and wear loss of the Fe-Cr-Ti-C hardfacing alloys. With the increasing of boron, the hardness of the hardfacing alloys increases and it results in the improvement of their wear properties.

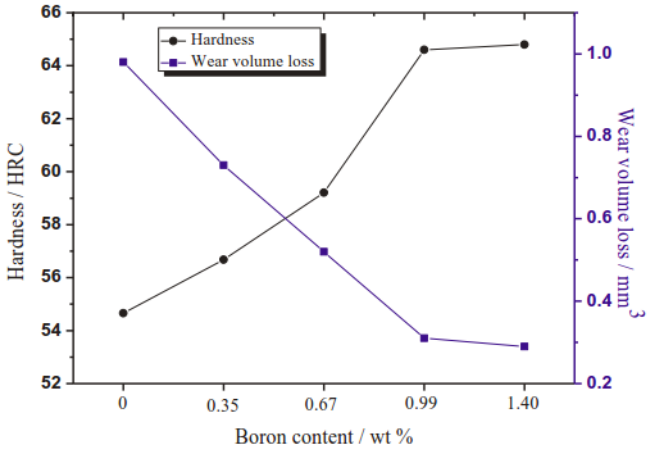


Figure 25: The effect of boron on the hardness and wear loss of the Fe-Cr-Ti-C hard-facing alloys. [59]

In fact boron increases the activity of carbon in the molten alloy, and its effect is like some amount of carbon is added to the molten alloy.[59] Carbon addition reduces the eutectic temperature for iron base alloys based on the following equation. [60]

T_E=1232-1926C+351Cr

As a result of the decrease in the eutectic temperature, the primary proeutectic carbides have more time to grow. Moreover, the CVF of five samples are 14.10, 18.67, 23.99, 29.87 and 36.00%, respectively. This is because boron atoms embed into the crystal lattice of M_7C_3 carbide and form $M_7(C,B)_3$ and as a result carbide diameter increases from 9 to 20 µm. [59]

Carbide volume fraction (CVF) has a key role in obtained hardness of high chromium hardfacing alloys. In another research, the effect of CVF was investigated, in this study the CVF was changed by changing the shape of carbides in different coatings while the amounts of carbides were constant in all of them. This change in carbide shape and as a result its volume fraction in coating was done by changing the process parameters. These coatings were deposited by using plasma transferred arc cladding (PTAC) process and morphology of carbides were changed by electromagnetic stirring (EMS).

The following table shows the chemical composition of Fe-based alloy powder.

Table 7: Chemical compositions of Fe-based alloy powder. [61]

Chemical compositions of Fe-based alloy powder	
C (wt.%)	4.8
Si (wt.%)	0.8
B (wt.%)	1.5
Cr (wt.%)	40
Fe (wt.%)	Balance

XRD results indicate that the coatings consist metastable carbide $(Cr,Fe)_7C_3$ and γ-Fe phase were produced. In fact in this hypereutectic alloy, proeutectic $(Cr,Fe)_7C_3$ is embedded in γ-Fe/$(Cr,Fe)_7C_3$ eutectic phase. [61]

Without stirring, the average size of $(Cr,Fe)_7C_3$ carbide is 73 µm, and it has the strip-like shape which does not show high volume fraction. But after changing the process parameter (increasing stirring current), the shape of carbides changed to rosette-like which shows higher volume fraction and higher hardness was achieved. Increasing stirring current to 3 A, resulted in generation of hexagonal blocky carbides with 20 µm size which were distributed uniformly in the coating. This hexagonal shape of carbides result in the maximum amount of volume fraction compared to strip-like or rosette-like carbide shape. The maximum hardness of coating which, 1050 HV, was obtained in this condition. [61]

This study suggests that the highest hardness and excellent wear resistance were obtained when hard carbides have the maximum volume fraction. In this study in a constant amount of carbide , the maximum volume fraction was achieved when carbides had hexagonal shape compared to Strip-like or rosette-like shapes pf carbides.

6.9 Tool steel

Cold work tool steels containing high chromium and high carbon are widely used in mineral processing industries because of their high hardness and high wear resistance. [62]

In a study, cold work tool steel coatings with a thickness up to 2 mm were deposited on bond coated low carbon steel substrates for wear resistance evaluation and investigation. In fact the objective and aim of this study is to develop thick high chromium containing cold work steel coatings deposited by HVOF spray processes and evaluating their wear resistance.

The following table demonstrates the chemical composition of cold work tool steel powder.

Table 8: Chemical composition of cold work tool steel powder. [62]

Chemical composition of cold work tool steel powder.

Alloying element	C	Mn	Si	Cr	Mo	V	Fe
Wt. %	1.90	0.30	0.60	20.0	1.00	4.00	bal.

Phase analysis reveals that the powder feedstock is composed of retained austenite and M7C3 (chromium rich) eutectic carbides as the main microstructural constituent. This is niormally referred as eutectic mixtures of high temperature phases retained because of rapid solidification during atomization. This exhibits that powder is a hypoeutectic cold work tool steel. [62]

Phase analysis of coating indicates that coating consist martensite and retained austenite along with eutectic carbides. [62]

Hardness of 712±31 HV0.05 was achieved in this HVOF sprayed cold work tool steel. This is relatively high hardness and in fact the cold work tool steels are known for their high hardness and therefore they are used in many wear resistant applications.

A pin on disk test was performed to examine the wear resistance of thick cold work tool steel coatings on different types and sizes of abrasive wear. Abrasive wear resistance test of the cold work tool steel coating against different kinds of abrasive papers (SiO_2,and Al_2O_3, SiC) with different mesh sizes (80 and 220) was done. To compare the abrasive wear resistance of the cold work tool steel coating, abrasive wear resistance of a standard high speed steel (HS6-5-3) pin has been included in the results. The results can be seen in the following figure.

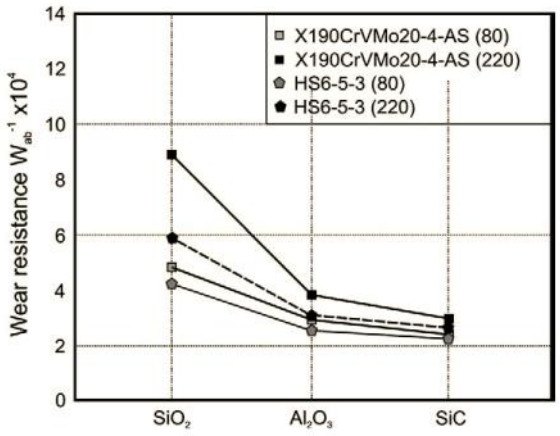


Figure 26: Abrasive wear resistance of the cold work tool steel coating against different kinds of abrasive papers (SiO_2,and Al_2O_3, SiC) with different mesh sizes (80 and 220). HS6-5-3 represents standard high speed steel pin. [62]

As it can be seen from the results the HVOF sprayed cold work tool steel coating displayed a relatively high wear resistance compared to the HS6-5-3 pin. This can be related to the fine grained microstructure of coatings with a large volume fraction of hard carbides that exist in martensitic/austenitic iron-base phase. [62]

The result of this study suggest that the cold work tool steel coating displays a superior abrasive wear resistance against soft and fine abrasive and their abrasive wear resistance against hard and coarse abrasive is comparable to high speed tool steels. [62]

6.10 Fe-B-C-Ti system

There is a high demand of materials for elevated temperature purpose. The results of some studies show that generally materials would lose their hardness when they are used in high temperatures and this makes them to not display good wear resistance.

In a study aimed to achieve a coating with high hardness in elevated temperatures, a mixture of Fe-Ti-B-C alloy powder (Table 9) and B_4C powder were coated on a mild steel substrate by plasma-transferred arc (PTA). The composition of mixture is 80 Fe-Ti-B-C + 20 B_4C. In addition another type of coating with 80 Fe-B-C +20 B4C was deposited to compare the results. Coating deposited by Fe07 (0.45 C, 4.5 Cr and the Fe balance) was used as reference coating. [64]

Table 9: The nominal compositions and characteristics of the used powders. [64]

The nominal compositions and characteristics of the used powders

Powders	Composition (wt.%)						Melting point (°C)	Density (g cm^{-3})	Size (μm)
	Ti	C	B	Al	Si	Fe			
Fe–Ti alloy	21.07	3.80	–	2.50	3.10	Balance	1085	6.15	≤150
B_4C	B ≥ 76% , dissociated C ≤ 2.0%						2450	2.52	≤50

Thermal stability test was done to evaluate the high temperature behavior of Fe-Ti-B-C coating. The temper resistance tests were done in order to check the thermal stability of the coating. Hardness of the coating was measure both in ambient temperature and in high temperature of 900 °C.

The following table demonstrates the test results of thermal stability.

Table 10: The test results of thermal stability. [64]

The test results of thermal stability

Alloy	Currents, A	Before tempering, HV	After tempering, HV
80 FeTi+20B_4C	160	911	918.3
80 FeTi+20B_4C	200	1069	979
80 FeTi+20B_4C	240	962.7	917
80 Fe+20B_4C	200	1185	926.7
Fe07	150	562	211

The results show that the coating obtained by Fe-Ti-B-C have much better temering resistance than the other coatings. XRD results indicate that the structure of coating contains TiB_2, FeB, and eutectic [Fe_3(C,B)+ Austenite]. In fact in high temperature most of the eutectics were decomposed and disappeared in the microstructure but TiB_2, FeB phases remained in microstructure without change. It means that TiB_2 and FeB phases are more stable at elevated temperatures. Infact that's why Fe-Ti-B-C coating kept its hardness in high temperature because it's the only coating that has TiB_2 inside. So, it can be concluded that the increasing of the volume fraction of TiB_2 and FeB phases in coating can improve the coatings tempering resistance. [64]

6.11 Fe-Cr-Ni-B-C

Fe-Cr-Ni-B-C Colferoloy is indeed an interesting and promising alloy system for applications where corrosion and wear are involved. Several researches have been done by Professor Petri Vuoristo and his team in Tampere University of Technology, Tampere, Finland and cooperation with University of Modena and Reggio Emilia, Modena, Italy on coatings obtained by this powder after thermal spraying. [46, 66, 84]

Wear and corrosion resistance of coatings obtained by these powders and effect of different processing parameters, alloy system composition, blending of powder with hard ceramics and etc. on achieved properties of coatings were investigated during these researches.

Two fractions of the Colferoly 102- and 103-type powders were sprayed with both HVOF and HVAF, i.e., the coarser fraction being 53 µm and the finer fraction of 45 µm. Cr_3C_2- 25NiCr and WC-10Co-4Cr powders were sprayed with just HVOF process and were considered as reference materials. Base material used as substrate for coatings was EN 1.4307. Table11 shows the chemical composition of different powders and materials used in this study. [66]

Table 11: List of materials and coatings concerned. [66]

Name	Type	Fe	Cr	Ni	B	C
Colferoloy 102		Bal.	31	12	3.6	0.6
Colferoloy 103		Bal.	32	8	4.6	0.6
H.C.Starck Amperit 582.072	Cr_3C_2-NiCr	<0.5	Bal.	16-18.5	-	10-11.5
Sulzer Metco Diamalloy 5843	WC-Co-Cr	-	-	-	-	-
EN1.4307	A304	Bal.	17.5-19.5	8-10	-	-

Mechanical wear properties were tested with rubber wheel abrasion test and corrosion properties were evaluated by submerging the samples in corrosive chlorine solution with pH-value of 1.2 before tests. Corrosion tests were done at room temperature and at 50 ˚C.

The following figure demonstrates the hardness of coatings.

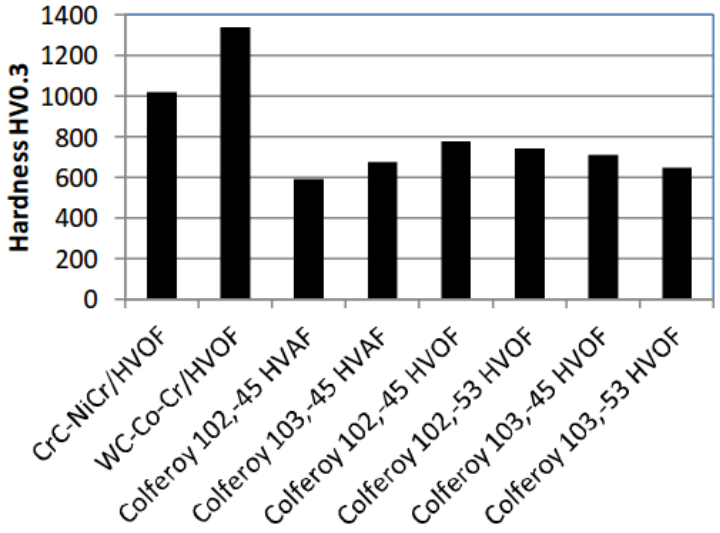


Figure 27: Average hardness of the coatings. [66]

Results show that wear resistance of the reference WC-CoCr and Cr_3C_2-NiCr specimens are over one magnitude better than the tested Colferoloy coatings. In fact the wear resistance of these reference materials are known to be the best and this is due to the existence of high volume fraction of hard carbides in the coating which are resistant to abrasion wear. As figure 28 demonstrates, the wear resistance of these Colferoloy coatings are in the same level as stainless steel which shows that these Colferoloy coatings do not show superior wear resistance.

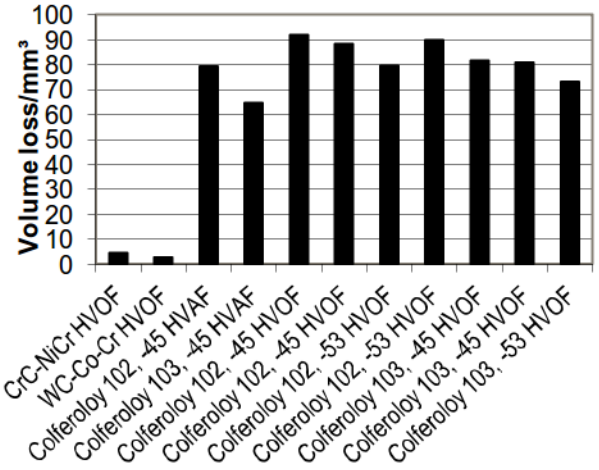


Figure 28: Results of the dry sand abrasion tests. [66]

Figure 29 shows the results of the corrosion tests.

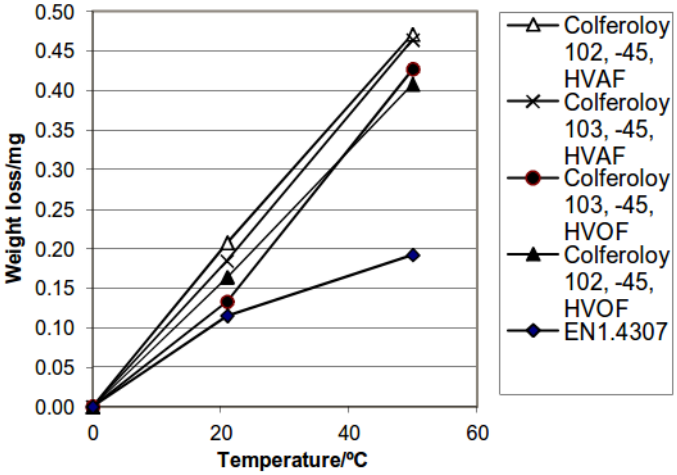


Figure 29: Results of the corrosion testing at elevated temperatures. [66]

Corrosion mechanism of the coatings was specified to be crevice corrosion inside the coating structures because of the penetration of corrosive electrolyte inside the pores and also non uniform distribution of the elemental components.

As it can be seen from Fig. 29 corrosion increase shows linear trend by increasing the temperature. In addition, HVOF sprayed coatings showed less weight loss compared to HVAF ones. This is in fact duo to the existence of less porosities in the structure of HVOF coated samples than HVAF ones. Less porosities result in less penetration of corrosive electrolyte and it means less crevice corrosion. These Colferoloy coatings exhibit inferior corrosion resistance compered to stainless steel. Porosities of coatings should be kept as low as possible to prevent crevice corrosion. Maybe sealing the coatings can be a good way to close the porosities so these Colferoloy coatings would dis-

play better corrosion behavior and property or maybe processing parameters should be optimized to produce uniform dense coating with high fraction of amorphous phase. [66]

The results of these studies suggest that thermal sprayed coatings obtained by Colferoloy 102 and 103 powders do not show abrasion wear properties comparable with WC-CoCr and Cr_3C_2-NiCr coatings and their corrosion resistance is worse than stainless steel in chlorine corrosive environments.

Another research was done by Giovanni et al. for better and deeper understanding of the tribological performance of these two Fe-Cr-Ni-B-C (Colferoloy) alloy coatings. This time coatings were just manufactured by HVOF thermal spraying process. Ball-on-disk (in room temperature and elevated temperatures) sliding wear and rubber-wheel dry particle abrasion test were done to evaluate the tribological performance of these coatings. Ni-Cr-Fe-Si-B-C and Cr_3C_2-25%NiCr coatings (also manufactured with HVOF), electroplated hard chromium and bulk tool steel were included in these tests to compare the results.

Following figure exhibits the results of hardness measurements.

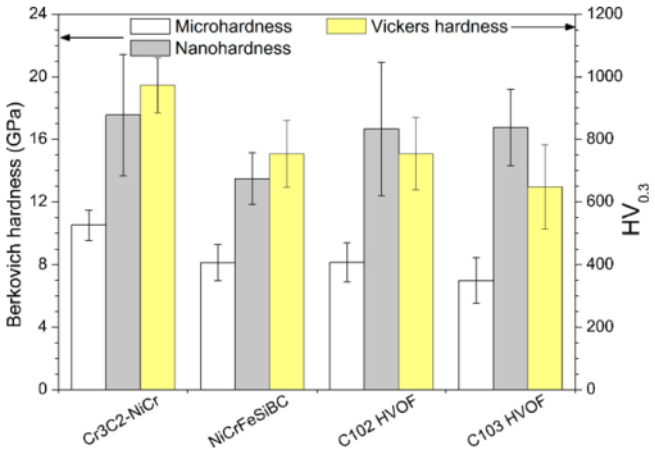


Figure 30: Berkovich micro- and nano-hardness abd Vickers hardness of thermally sprayed coatings. [46]

In room temperature wear tests against Al_2O_3 balls, the two Colferoloy coatings underwent similar wear rates, lower than those of the Ni-Cr-Fe-Si-B-C alloy but larger than those of the Cr_3C_2-NiCr cermet with diffrenece of almost one order of magnitude. The wear rates of the Colferoloy coatings were slightly larger than that of tool steel but lower than those of hard chromium platings. [46]

Table 12:Wear rates measured after ball-on-disk testing at room temperature. [46]

Coating	Sample wear rates ($\times 10^{-6}$ mm^3/(Nm))	
	vs. Al_2O_3	vs. 100Cr6
Colferoloy-102	8.67 ± 0.75	–
Colferoloy-103	12.08 ± 2.68	–
Ni–Cr–Fe–Si–B–C	42.37 ± 1.59	18.79 ± 1.26
Cr_3C_2–NiCr	2.80 ± 0.13	–
Hard chromium #1 ($HV_{0.5}$ = 894 ± 19)	120.70 ± 20.42	7.30 ± 1.35
Hard chromium #2 ($HV_{0.5}$ = 900 ± 13)	53.92 ± 9.20	5.23 ± 1.69
Tool steel	6.00 ± 0.23	0.27 ± 0.09

When the test temperature was increased, the ranking between the wear resistance stayed the same. The two Colferoloy coatings underwent similar wear rates, lower than those of the Ni-Cr-Fe-Si-B-C alloy but larger than those of the Cr_3C_2- NiCr cermet.

The following table shows the result of abrasion tests done on Colferoloy coatings and reference Cr_3C_2- NiCr cermet coating.

Table 13: Weight loss of the Colferoloy coatings and of the reference Cr_3C_2- NiCr cermetcoatings. Recorded at the end of the 1-h long rubber wheel abrasion wear test. [46]

Weight loss of the Colferoloy coatings and of the reference Cr_3C_2–NiCr cermet coating, recorded at the end of the 1-h long rubber-wheel abrasion wear test.

	Coating		
	Colferoloy-102	Colferoloy-103	Cr_3C_2–NiCr
Weight loss (mg)	677	584	31

It is clearly seen that that Colferoloy coatings show huge amount of wear during abrasion wear test. These results are coincident with the results of previous study done on these coatings in Tampere University of Technology, Tampere, Finland.

The higher nano-hardness of the Colferoloy coatings means that these coatings have higher intrinsic mechanical strength at intralamelar level. This is beneficial for resistance against abrasive grooving by small hard asperities (i.e. asperities which produce abrasive grooves smaller than the lamella size as it occurs in sliding wear) and reduces the tendency toward adhesive wear. On the other hand, the Colferoloy coatings exhibit large gap between nano- and micro hardness, which can indicate poorer interlamellar cohesive strength and this justifies their higher tendency toward delamination. When the size of the abrasive is larger than the lamella size, as it is the case in the rubber-wheel dry particle abrasion test (grooves larger than lamella size), the intralamellar mechanical properties (nanohardness) becomes less important and the behavior is more dependent to large-scale mechanical behavior(micro-hardness) . This gap between nano hardness and micro hardness in Colferoloy coatings explains why these coatings show poor abrasion wear. [46]

In general, the better sliding wear performance of HVOF-sprayed metal alloys over electroplated chromium and Ni-based thermally sprayed coatings suggest that these coatings can be used in sliding wear applications but these Colferoloy coatings are not suitable for dry particle abrasion conditions.

Further studies done by Bolelli et al. on these Fe-Cr-Ni-B-C coatings investigates the effect of WC-Co powder addition on mechanical behavior of these coatings. The Fe-alloy feedstock powder was therefore blended with 0, 20 and 40 wt.% of WC-12 wt.% Co powder and sprayed by both HVOF and HVAF methods. The results show that the reinforced Fe- based coatings with WC-Co show more than order of magnitude wear resistance compared to unreinforced ones in both abrasion and sliding tests. Substantial reinforcing effect of WC-Co phase is observed at room temperature. Result show that at higher temperatures of 400°C and 700°C, the strengthening effect of WC-Co becomes less significant and this is probably because of the thermal softening and oxidation that occurs in WC-Co. [85]

In addition, effect of different coating processing methods on obtained coating properties was also evaluated in this research. Thermal alterations during the HVOF process result in hardening of splats. WC-Co splats would harden duo to the formation of W_2C and Fe-based splat would harden because of grain refinement and formation of amorphous solid solution phase. These result in higher nano hardness of HVOF sprayed coatings (Intralamellar strength) than HVAF sprayed coatings. [85]

The results of this study suggest that coatings obtained by blending of WC-Co powders to Fe-Cr-Ni-B-C powders exhibit better wear performance than non reinforced Fe-Cr-Ni-B-C ones and this makes them more comparable materials with WC-Co coatings.

In another research done by Milanti et al. effect of addition of molybdenum and blended hard material on cavitation erosion wear and corrosion resistance of coatings obtained by these Colferoloy powders were investigated. In fact four different powders were selected for this study. In addition to Fe-Cr-Ni-B-C powder (Colferoloy), three customized powder formulations were designed for enhancing the coating properties by adding Mo in the chemical composition and by blending hard WC-Co powders with the original Fe-based powder composition. These powders were coated by HVOF thermal spraying method on low carbon steel plates. The following table demonstrates the nominal composition of powders in weight percent. [84]

Table 14: Nominal composition of powders in weight percent. [84]

Powder	*Fe*	*Ni*	*Cr*	*Mo*	*B*	*C*	*WC-Co 88-12*
C102	bal.	12	31	/	3.6	0.6	/
C102(Mo)	bal.	12	31	2	3.6	0.6	/
C102(20)	bal.	12	31	/	3.6	0.6	+ 20wt.%
C102(40)	bal.	12	31	/	3.6	0.6	+ 40wt%

Electrochemical results show that, the addition of WC-Co powder into the experimental coatings C102(20) and C102(40) resulted in an increase of corrosion potential and de-

crease of corrosion current. In addition, the higher the WC-Co content the nobler are the coatings and the corrosion current is lower. The powder with Mo addition exhibits similar trend (lower corrosion current and higher corrosion potential). Furthermore, Mo addition resulted in the coating passivation over a wide range of potential (-300 mV to 1000 smV). It can also be discussed in this way that addition of hard WC-Co particles can result in denser coatings with less porosity duo to the effect of their impacting on ductile Iron-based coating and this result in better corrosion properties. [84]

Based on the results, Fe-based coatings are reported to have higher cavitation erosion resistance compared to WC-CoCr and Ni-Cr-Fe-Si-B-C. In particular addition of Molybdenum (Mo) resulted in higher cavitation erosion resistance. However the two Fe-based coatings obtained with hard WC-Co particles addition are reported to have worse overall cavitation resistance. This is probably duo to the outstanding combination of high hardness, high density, high elasticity, work-hardening ability, and the induced martensite transformation which makes the coatings obtained by these Fe-based powders resistant against cavitation erosion. In fact elasticity of the coating plays a key during cavitation erosion applications and results show that addition of hard WC-Co particles decrease the elasticity of coating. In addition, hard WC-Co particles that are pulled out from coating during cavitation erosion can lead to more erosion by further impacting of the coating. [84]

The results of this study suggest that Fe-Cr-Ni-B-C Colferoloy material can be used as coating or even bulk material for hydraulic applications where pressure is constantly changing but addition of hard WC-Co powders makes their cavitation resistance properties worse, in contrary with the effect of the addition these hard particles on abrasion and sliding wear.

6.12 Fe-based amorphous coatings

Bulk metallic glasses (BMGs) or amorphous alloys have completely different structure than crystalline metals. They are well known because of providing high strength and high hardness, large elastic limits and furthermore outstanding corrosion and wear resistance. Bulk metallic glasses (BMGs) are metastable metallic materials with disordered atomic structure, these result in unique and outstanding properties obtained by them. A great deal of efforts have been offered to the development of alloy systems with high glass forming ability (GFA) and to study of glass formation theory and also the origins for the outstanding properties of these materials. A number of BMG products are used in structural applications duo to high diameter of BMG achieved in the process. But bulk metallic glasses have poor ductility in room temperature that's why they cannot be used in industry in a large scale and their industrial application of Bulk metallic glasses is little. Amorphous coatings as alternative forms of BMGs prepared by thermal spraying, not only overcome the intrinsic brittleness of the alloys, but also carry forward the superiority in corrosion and wear resistance showing great potential for industry application. In fact amorphous coatings based on BMG systems have received increas-

ing attention during recent years because of the combination of the excellent properties inherited by bulk amorphous alloys and the potential industrial application for amorphous coatings. [4,44]

Among various BMG systems amorphous coatings based on Fe-based BMG systems are more attractive because of the combination of good properties, good glass forming ability and relatively low material cost and also their high crystallization temperature. Fe-based amorphous coatings not only showed excellent ability to resist localized corrosion in acid, alkali and salt solutions, but also exhibited superior wear resistance than mild steels, hard Cr and Al2O3 coatings. [4,44]

There are some requirements for achieving amorphous coatings. If the cooling rate of the coating is high enough so the temperature of the deposited coating is lower than glass transition temperature the n there is probability to achieve amorphous phase. During thermal spraying after deposition of particles onto substrates, the particles start to cool down by the rapid cooling rates (104 to 106 $^{\circ}$C per second). This high amount of cooling rate results in existence of several non-equilibrium phases (amorphous or nanocrystalline) in a single coating. High cooling rate prevents the atomic diffusion and in fact doesn't give enough time to atoms to go to their crystalline lattices and as a result inhibits the crystal formation. In fact in thermal spraying processes the necessary time for solidification is between 10^{-8} and 10^{-6} seconds. This short solidification time is the result of radial spread of particles, and the increase in surface area of particles after their impact to the substrate.

If just high cooling rate is applied then the obtained coating would have crystalline structure with some proportion of amorphous and nanocrystalline phase inside. Some other requirements other than high cooling rate should be applied to ensure achieving a coating with high amount of amorphous content. Glass forming ability of deposited material has the key role to achieve amorphous coating. (1) The alloy system should be multi component (2) There should be large difference between the atomic radiuses of different components in the alloy system. (3) There should be large negative energy of mixing between each two pair of components. This large negative energy of mixing between each two pair of elements causes a short range order in the structure and as a result prevents crystal structure formation. These three requirements mentioned above are called glass forming ability (GFA) of an alloy system .To get amorphous structure from an alloy system after deposition in thermal spraying, that system should have high glass forming ability (GFA) and be cooled in high rates. [4,44]

In this report, the recent progress of the Fe-based amorphous coatings is summarized.

Fe48Cr15Mo14C15B6Y2 is one kind of this alloy system with high GFA. Fe48Cr15Mo14C15B6Y2 amorphous coating are spontaneously passivized in 3.5% NaCl, 1N HCl and 1N H_2SO_4 solutions and do not suffer pitting corrosion so they can

be used in marine and acidic environments to prevent corrosion. However these coatings do not show good results in alkaline environmentsThe dry sliding wear behavior of Fe48Cr15Mo14C15B6Y2 amorphous coatings was significantly lower than electroplated chromium and Al_2O_3 coating. [67,68]

Farmer and Branagan reported that Fe49.7Cr17.7Mn7.4Mo1.6W1.6B15.2C3.8Si2.4 amorphous coating deposited by HVOF is more resistant to pitting corrosion than nickel based alloy(C-22) coating in seawater solutions and the salt fog environments. The coating shows hardness over 850 HV which is comparable to Cr_3C_2-NiCr coatings. In addition the coating exhibits good wear resistance with the weight loss approximately 5 times less than that of the steel substrate due to the high hardness.[69,70]

Fe-Cr-B-Si-Mn-Nb-Y alloy system has very strong GFA, which satisfies the three empirical glass forming rules. (1) Multicomponent alloy systems which consists of more than three components. (2) Significantly different atomic size ratios above 13% (Y>Nb>Cr>Mn>Fe>Si>B) and (3) negative heats of mixing among the constituent components. In addition, B and Si are self-fluxing elements in this system which results in coatings with low amount of porosity. The coating shows superior wear resistance compared to 3Cr13 coating and substrate. The wear resistance of the amorphous coating obtained by this system is 7 and 2.3 times better than substrate and 3Cr13 coating .The Fe64.82Cr9.23B20.69Si1.9Mn1.01Nb1.8Y0.55(at %) is an example of this alloy system. [71]

SHS7170, SHS8000, FeCrBSiMnNbY, FeCrBSiNbW and FeBSiNb metallic glass coatings show good elevated-temperature erosion wear resistance so they can be used for boiler applications.. When they are heated to temperatures above their crystallization temperature, structure with nanoscale grains are produced which have really high hardness. The SHS7170 alloy is an eight element glass forming alloy which contains by wt% chromium (20-25), molybdenum (less than 10), tungsten (less than 10), boron (less than 10), carbon (less than 5), silicon (less than 5), manganese (less than 5) and base iron. The amorphous coating obtained by SHS7170 alloy is used in boiler applications. The temperature of the boiler is approximately around 700 Celsius degrees. Because boilers operate at high temperature and actually above crystallization temperature of SHS7170 alloy, this potential for coarsening and the resulting deleterious changes in properties exists. This concern was studied. The microstructure of the heat-treated SHS7170 wire-arc coating is shown by TEM. The TEM image shows that in 700 Celsius degrees after 10 minutes heat treatment, the microstructure is completely crystalline. The starburst morphology of the crystallites that was seen previously has changed into a uniform equiaxed nanocomposite microstructure with phase sizes ranging from 60 to 110 nm. This transform in structure of coating didn’t scarify any of the coating properties because coarsening has not happened and grains are in nanoscale. [72,79]

Fe41Co7Cr15Mo14C15B6Y2 shows good corrosion resistance in different electrolytes of HCL, HNO_3, NaOH and 3.5% NaCl aqueous solutions. The results show that the corrosion resistance of this alloy in 3.5% NaCl solution is superior to the other three solutions.[73]

Fe64.82B20.69Cr9.23Si1.9Mn1.01Nb1.8Y0.55 (at%) amorphous coating shows superior sliding wear resistant compared to 3Cr13 martensitic stainless steel coating. under the same wear testing, the volume loss of crystalline 3Cr13 coating is much higher than that of metallic glass coating. this indicates that metallic glass coating has better resistant to wear. [74]

FeBSiNb metallic glass coating shows excellent abrasive wear resistance. The relatively wear resistant of amorphous coating is about three times more than 3Cr13 coating. [75]

FeCrBSiNbW coatings were produced by twin wires arc spraying system. The microstructure of the coating includes amorphous matrix which contains α-(Fe,Cr) nanocrystaline grains with diameters ranging from 20 to 75 nm. This amorphous coating shows appropriate wear and corrosion resistance

The amorphous coating has higher H/E ratio compared to 3Cr13 coating which results in better wear behavior of amorphous coating.[76]

The as sprayed coating of Fe-10Cr-10Mo-8P-2C (mass percent) that is composed of 100% amorphous phase structure has excellent corrosion resistance in 1N H_2SO_4 and 1N HCl solutions.[77]

FeCrNiB alloy system can be used to produce amorphous coatings which show excellent corrosion resistance in different kind of environments. They can be used as an example in different applications used in chemical industries and oil refineries to resist aggressive environments. [78]

The combination of high boron content and good corrosion and wear resistance makes Fe49.7Cr18Mn1.9Mo7.4W1.6B15.2C3.8Si2.4 amorphous coating promising for being used in under-ground applications like the storage of spent nuclear fuels.[70]

Self-cleaning, anti-icing, anti-fouling, anti-corrosion surfaces are some practical applications of superhydrophobic surfaces. Some artificial super hydrophobic surfaces have been produced by mimicking the surface structure in the nature such as lotus leaf, water strider and butterfly. These superhydrophobic surfaces are generally made from polymers and polymers are not robust enough to show good wear resistance. Thermal spraying of amorphous metallic coatings is a way to get hydrophobic surfaces which exhibit super-high hardness and excellent corrosion resistance so they can be used in different industrial applications.[80]

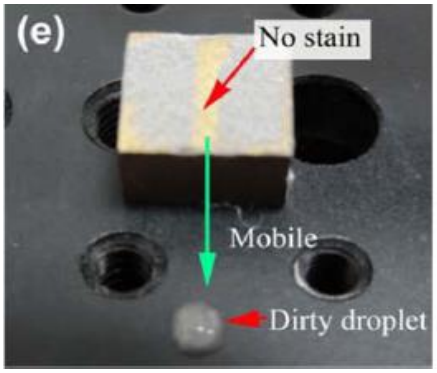


Figure 31:Self-cleaning effect of hydrophobic amorphous coatings [80]

These Fe-based metal alloy coatings that are discussed till now, although being good alternatives for electroplated chromium and other thermal sprayed metal coatings do not show comparable wear resistance with cermets such as WC-Co. Cermet powders with iron-based matrix can be a solution for this issue. Sometime also hard ceramic powders can be blended with Iron-based powder and deposited on coating. In this report, the recent progress of the Fe-based cermet coatings is summarized.

6.13 Fe-based matrix/TiC

FeCr-TiC powder was used to produce coatings which can be comparable with conventional cermets. In this powder Fe-20 wt.%Cr was the binder phase and TiC was the hard ceramic phase. The coating proeduced contained the following phases: titanium carbide, an iron-titanium intermetallic, an iron-rich body-centred cubic binder phase and iron-titanium oxides. Results show that the coatings produced in this work exhibited abrasion wear rates equivalent to or lower than coating produced by blended NiCr-Cr_3C_2 powder. [81]

In another research, TiC-strengthened Fe-based powder with composition that is mentioned in the following table was used to produce coatings.

Table 15:Composition of TiC-strengthened Fe-based powder [82]

Hard phase 33% TiC, wt.%	Matrix 67%			
	C, wt.%	Cr, wt.%	Mo, wt.%	Fe
100	0.75	13.50	3.00	Bal.

The feedstock powder consisted 33wt.% TiC hard phase and 67 wt.% Fe-based matrix. The microhardness in the as-sprayed condition was 714 HV. Further heat treatment resulted in an increase of 130±80 HV in hardness. [82]

Sliding wear behavior of these coatings was compared with NiCr-Cr_3C_2 with pin on disk test. Comparing the wear volumes of the different coatings, it can be concluded

that the coating produced with agglomerated and sintered Fe/TiC powder show similar wear behavior as HVOF sprayed Cr_3C_2-NiCr (80/20) coating. [82]

This research suggests that there would be significant raw material cost save by using Fe/TiC material compared to Cr_3C_2-NiCr with similar sliding wear behavior. [82]

6.14 Fe-based matrix/CrB_2

Powders with high alloyed steels as matrix materials and incorporated hard CrB_2 particles were HVOF sprayed. By using the HVOF spraying, the microstructure of powder can be transferred to the coating. The deposited coating displays low porosity and high microhardness values of around 1000 HV0.3. These coatings exhibit high abrasion wear resistance and this makes them an appropriate candidate to be used as an alternative to hard electroplated chromium coating. This can have application in paper industry.

Addition of reinforcement particles leads to a decrease of the amorphous phase portion in the sprayed coatings, because the reinforcement particles act as crystallization nuclei which hinder the melt from deep undercooling and amorphous solidification. But these hard particles in coating would be beneficial in coating because these precipitations prevent the washing-out of the matrix.

Results show that the wear volume of reinforced coatings is twice lower than that of Fe-based coating without reinforcing hard particles inside. In addition the results show that although the values of the wear resistance of HVOF sprayed WC/Co coating is not reached, the behavior of these coatings is better than electroplated chromium. [83]

6.15 WC-FeCrAl

WC-15%FeCrAl alloy system is another system that sounds to be promising potential for being substituted and replaced to conventional WC-CoCr material. Effect of different thermal spraying processes and parameters on the obtained properties of coatings were studied. [86-87]

Initially they were deposited by liquid-fuelled HVOF torch (with different oxygen/fuel ratio) and they were compared with reference coating of WC-CoCr. HVOF-sprayed WC-15 wt.%FeCrAl (agglomerated and sintered powders) layers were therefore produced using different oxygen and fuel (kerosene) flow rates and their mechanical and tribological properties were compared to HVOF-sprayed WC-10 wt.% Co-4 wt.%Cr.

Results show that during liquid-fuelled HVOF thermal spraying, both WC-CoCr and WC-FeCrAl powders, will be in be in some extent oxidized and decarburized. In fact WC-FeCrAl show more thermal alteration and this is because of the higher oxidation tendency of FeCrAl matrix compared to CoCr one (probably because of the large reactivity between Al and oxygen at high temperatures). Indentation testing shows that the

hardness of the WC-FeCrAl coatings were between 1000 HV and 1100 HV and their modulus was around 200 GPa. WC-CoCr reference showed average hardness of 1200 HV3N and elastic modulus of 350 GPa. [87]

Effect of Oxygen-fuel ratio used during liquid-fuelled HVOF thermal spraying of WC-FeCrAl powder was tested. More decarburization and less oxidation occurred in particles during their thermal spraying when lower oxygen-fuel ratio was used in the process and more oxidation and less decarburization occurred in particles when higher oxygen-fuel ratio was applied during the process. In fact coatings sprayed with low oxygen-fuel ratio exhibit better interlamellar cohesion because of less amount of oxidation around particles, but they exhibit lower elastic stiffness because they are more decarburized compared to coatings obtained with higher oxygen/fuel ratio.

The best mechanical behavior would be obtained in the coating with the highest amount of H/E ratio. As Bolelli explains, the parameter H/E indicated the ability of the material to accommodate strains within elastic deformation regime, without reaching the yield or failure limit. When the H/E ratio is higher, the coating can accommodate larger strain before the strain exceeds that elastic limit. This H/E ratio has key role specially in coating which show brittle behavior because in these conditions after the elastic limit the coating would fracture immediately without any plastic deformation. The results show that WC-FeCrAl coatings exhibit brittle behavior. In this study the highest H/E ratio can be obtained by optimizing the oxygen-fuel ratio. [87]

In general, the results show that obtained WC-FeCrAl coating with high H/E ratio can be a good alternative for WC-CoCr reference in sliding wear resistant applications such as protection of shafts, bearing, seals, piston sleeves, etc. However these coatings do not show appropriate performance during abrasion wear in any condition of coating. [87]

To evaluate the effect of different thermal spraying methods on obtained properties of coating ,powders of this material were deposited by different thermal spraying methods. They were deposited by liquid-fuelled HVOF thermal spraying, gas-fuelled HVOF and M2-HVAF thermal spraying. Then WC-FeCrAl powders were deposited by gas-fuelled HVOF and also HVAF processes. Two different torches of JP5000 and DJ2700 are used in gas-fueled HVOF spraying.

The results show that different thermal spraying processes have significant effect on the obtained properties of the coating.

The results of these studies indicate that different torches used in gas-fuelled HVOF thermal spraying have different effects. The results show that compared to the JP5000-HVOF torch, the DJ2700 one result in less extensive melting and oxidation and thermal alteration of WC-FeCrAl powders. In fact coating obtained by DJ2700 is comparable with liquid-fuelled HVOF coating. In the present case since the JP5000 torch is operated with excess oxygen whilst the DJ2700 one is operated with excess fuel, the gas jet of

the DJ2700 probably contains lower amounts of oxygen. In addition, models show that the in flight particle temperatures produced by these two torches are not significantly different. The main difference between these torches is that, the nozzle length and the stand-off distance are much lower in DJ2700-HVOF compared with JP5000. These result in the lower degree of oxidation and decarburization of particles during DJ2700-HVOF compared to JP5000 duo to shorter times of particle travel in this process and makes it comparable with liquid-fuelled HVOF spraying process. However duo to the higher velocity of particles during JP5000 thermal spraying, higher magnitude of compressive stress was obtained in the coating. On the other hand coatings obtained by M2-HVAF thermal spraying resulted in no significant thermal alteration of the powders as particles remained almost in solid state during deposition but probably because of the poor optimization of processing parameters, high amount of porosity was produced in obtained coating. [86]

The micro- and nano-hardness values of all sprayed WC-FeCrAl coatings are so broad. This can be duo to the oxidation and thermal alterations that occur around the splats and result in poor bonding of splats or it can be as the result of the intrinsic feature of the WC-FeCrAl material. Interlamellar cohesion in sprayed coatings depend significantly on plastic deformation at the interface between impinging particles and underlying coating layers. WC-FeCrAl do not show high plastic deformation and it prevents the bonding of splats. Another reason of gap between nano hardness and microhardness of these coatings can be duo to the presence of WC in FeCrAl matrix which result in a kind of inhomogeneity. [86]

At room temperature, the wear behavior of all WC-FeCrAl coatings, both under dry sliding conditions and under particle abrasion condistion, is controlled by brittle cracking. The extend of brittle cracking depends on the processing method used to produce coating and wear and tribological conditions. Coatings obtained by JP5000 HVOF spraying and by HVAF spraying experience more microcracking, this is duo to the larger thermal alteration or to higher porosity that exist in these coatings respectively. Moreover, much larger cracks and more severe delamination are produced under dry particle abrasion conditions than sliding conditions and this is because of the larger size of the abrading particles which would affect the coating in larger scale and make the microhardness of coating an important factor. [86]

The dry sliding wear resistance of the DJ2700-HVOF sprayed WC-FeCrAl which exhibit lower gap between micro- and nano-hardness compared to other thermal sprayed coatings , duo to higher cohesion between splats which is the result of less particle oxidation and thermal alteration in this process compared to other HVOF sprayed ones and porosity compared to HVAF sprayed one, is comparable with reference WC-CoCr coating in low temperatures. But in dry abrasion conditions, the WC-FeCrAl coatings do not show comparable results with reference coating. In addition, in higher temperature, sig-

nificant oxidation of WC-FeCrAl coating makes these coatings not suitable for being used in dry particle abrasion or sliding conditions. [86]

The results of these studies suggest that by using appropriate thermal spraying method and optimizing parameters, it is possible to obtain coatings for room temperature sliding applications comparable to WC-CoCr coatings from WC-FeCrAl powders but these coatings do not show comparable results during high temperature and also abrasion wear applications.

7. EXPERIMENTAL PART

Practical part of this work covers the results which are obtained from characterization of different coatings produced by high velocity air-fuel (HVAF) thermal spraying from (Fe,Cr)C-30FeNiCrSi (Amperit 575.074) powder. As it is mentioned in the introduction, the aim of this part is to understand the effect of different processing parameters such as air-fuel ratio and nozzle type on the obtained properties of the coatings and finding out the optimum processing parameters. Minitab statistical software was used for finding out the best combination of parameters that should be used during thermal spraying to obtain the desired property such as hardness or thickness in the coating.

More details of the parameters and Minitab software are discussed in the next following parts.

7.1 Materials and Methods

7.1.1 Powder

Since the particle size, shape, composition and phases of the powder play a key role in the microstructure of the thermal sprayed coating, at first different characterization tests were done on the powder.

Particle size distribution was studied by laser diffraction method using wet dispersion technique (Sympatec laser diffraction system). The microstructural investigation of powders (morphology and cross-sections) was carried out by Scanning Electron Microscopy (SEM, Philips XL30) equipped with energy dispersive X-ray (EDX) microanalysis. Phase composition was assessed by X-Ray Diffractometry (XRD, Empyrean, PANAnalytical, Cu-Kα radiation). Experimental conditions include 2θ range 20-120°, step size 0.02°, scan speed 0.02°/s, fixed incident beam mask 20 mm, anti-scattered slit fixed 1°, 8s revolution time sample, Nickel filter and PANAnalytical PIXcel 3D detector. Phase identification was performed using the PANAlytical X'Pert High Score Plus software using the ICDD JCPDF-2 database (International Centre for Diffraction Data, Newtown Square, PA, USA).

The following table and figures exhibits the characteristics of the powder.

Table 16: powder properties given by powder manufacturer

Powder	Manufacturing method	Particle size	Chemical composition weight %
Amperit 575	Agglomerated and sintered	-45 + 10 µm	70 (Fe,Cr)C / 30 Fe-NiCrSi

Results show that the size of the powders vary between 25-60 µm but they are unfortunately poorly dense. According to EDS analysis and XRD measurements, 70 (Fe,Cr)C / 30 FeNiCrSi was chemical composition of the powder. XRD results show that M_7C_3 and $M_{23}C_6$ (M can be Fe or Cr) make the chemical composition of the hard phase in powder which is 70 percent of the total composition. The remained 30 percent is austenitic steel with FeNiCrSi composition. Figure 32-35 demonstrate the powder morphology, particle size distribution, EDS spectrum, Powder cross section photo and XRD diffraction peaks of the powders

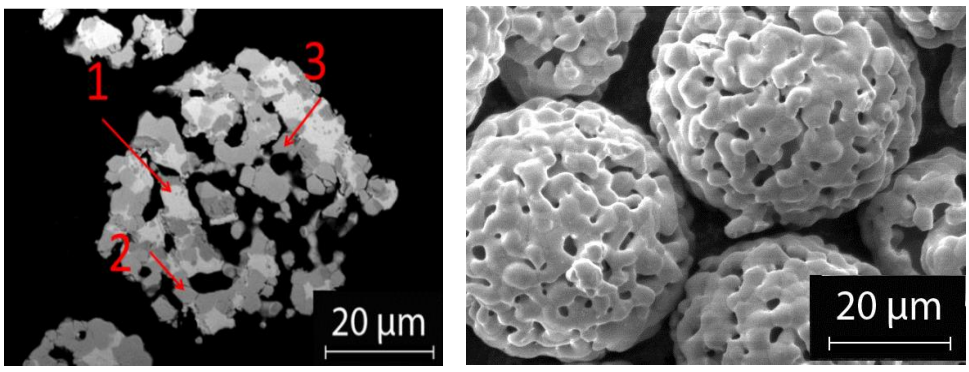


Figure 32: Powder cross section and morphology

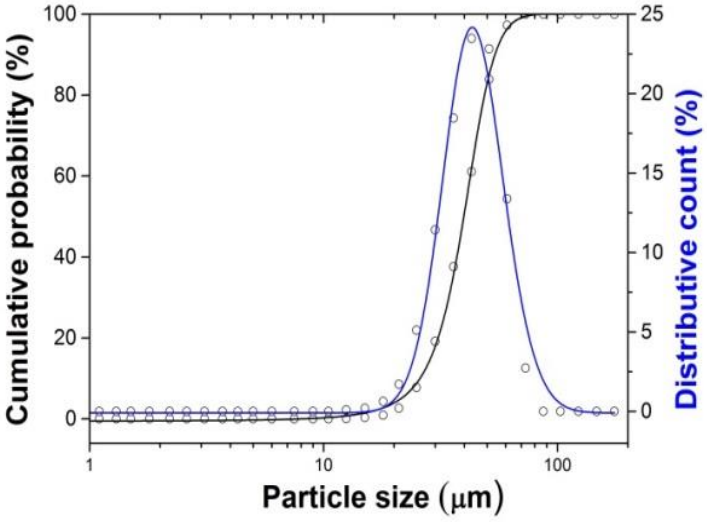


Figure 33: Particle size distribution

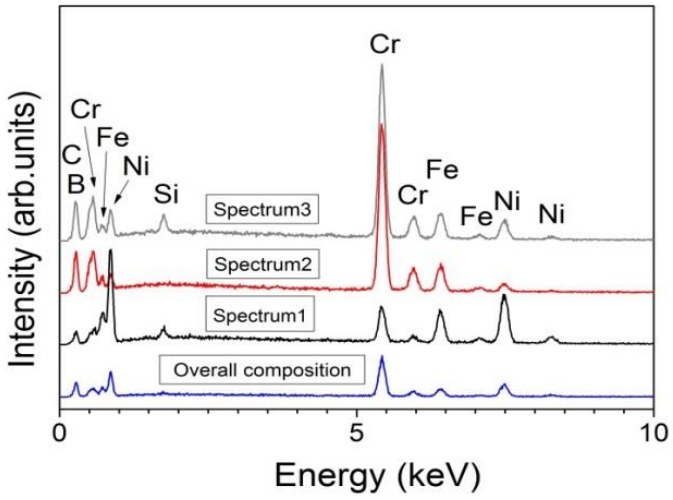


Figure 34: EDS spectrum of the powder

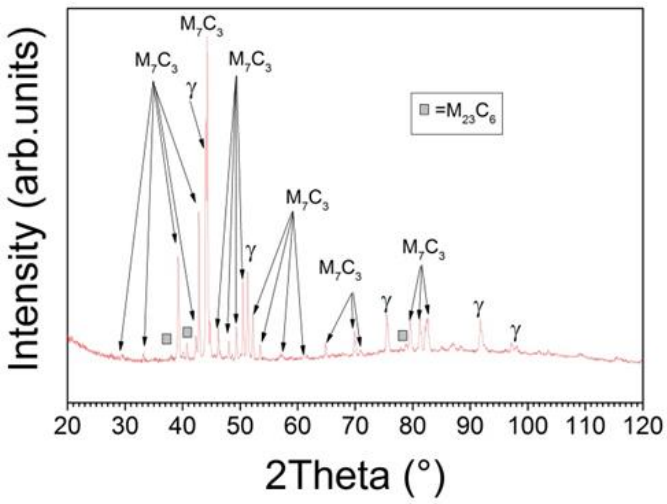


Figure 35: XRD diffraction peaks of the powder

7.1.2 Design of Experiment of the variable factors

For continuous improvement in product quality, it is necessary to understand the process behavior and variability and their effects on the products. In design of experiment, the researcher usually makes deliberate changes in the input factors and then observes and determines how the output functional performance responds accordingly. Design of Experiments (DoE) is a useful technique that is used for exploring processes, obtaining knowledge of the existing processes and their optimization. Design of experiments refers to the process of planning, designing and analyzing the experiment so finally valid conclusions are gained. Indeed, the objective of a DOE is to understand which set of variables in a process affects the performance most and in the next step determine the best possible levels for these factors to gain satisfactory output performance. [88]

In performing a designed experiment, we will deliberately change the variable processing factors in order to investigate corresponding changes in the output process and performance. [88]

In this experiment; air pressure, spray distance, flow rate, powder feeding rate are among the factors that are kept constant during the thermal spraying of powders. Their values can be found from the Table 18. On the other hand, nozzle type and $fuel_{1,2}$-air ratio are the parameters that are variant. In fact, these three parameters, nozzle type and fuel rate, have the most important role compared to other parameters on the obtained properties of the coating

Table 17:Spraying Parameters

#	Composition	Nozzle	Air [psi]	Fuel1 [psi]	Fuel2 [psi]	Injector	Carrier gas	Spraydist [mm]	Surf speed [mm/s]	Torch speed [mm/s]	Passes	Feed [g/min]
113	(Fe,Cr)C-30FeNiCrSi	4L4	108	105	105	1	60	300	750	750	8	100
114	(Fe,Cr)C-30FeNiCrSi	4L4	108	99	90	1	60	300	750	750	10	100
115	(Fe,Cr)C-30FeNiCrSi	4L0	108	105	105	1	60	300	750	750	6	100
116	(Fe,Cr)C-30FeNiCrSi	4L0	108	99	90	1	60	300	750	750	9	100
117	(Fe,Cr)C-30FeNiCrSi	4L0	108	99	105	1	60	300	750	750	8	100
118	(Fe,Cr)C-30FeNiCrSi	4L0	108	105	90	1	60	300	750	750	8	100
119	(Fe,Cr)C-30FeNiCrSi	4L2	108	105	105	1	60	300	750	750	8	100
120	(Fe,Cr)C-30FeNiCrSi	4L2	108	99	90	1	60	300	750	750	9	100
121	(Fe,Cr)C-30FeNiCrSi	4L2	108	99	105	1	60	300	750	750	8	100
122	(Fe,Cr)C-30FeNiCrSi	4L2	108	105	90	1	60	300	750	750	8	100
123	(Fe,Cr)C-30FeNiCrSi	4L4	108	99	105	1	60	300	750	750	9	100
124	(Fe,Cr)C-30FeNiCrSi	4L4	108	105	90	1	60	300	750	750	9	100
125	(Fe,Cr)C-30FeNiCrSi	4L2	108	102	97.5	1	60	300	750	750	8	100
126	(Fe,Cr)C-30FeNiCrSi	4L2	108	102	97.5	1	60	300	750	750	8	100
127	(Fe,Cr)C-30FeNiCrSi	4L2	108	102	97.5	1	60	300	750	750	8	100

Spraying the powders was done in Department of Materials Science, laboratory of Surface Engineering at Tampere University of Technology. Table 18 represents the spraying factors in more details. The following figure shows the specific HVAF gun that was used for spraying the powders.

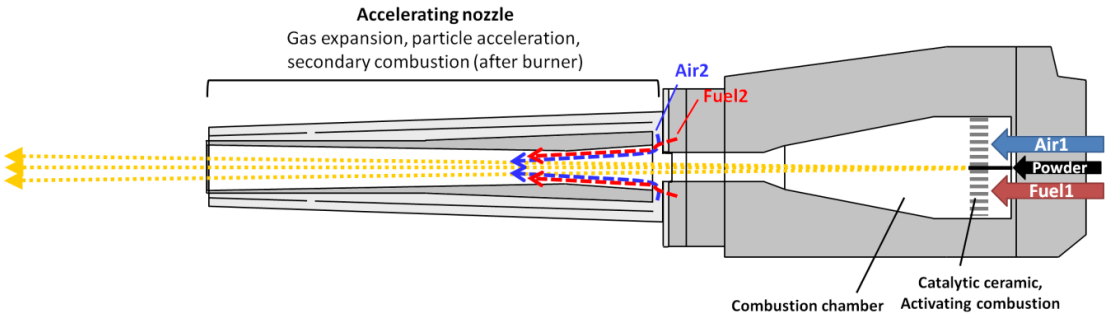


Figure 36: Supersonic Air Fuel HVAF (SAF) M3 gun [5]

4L4, 4L0 and 4L2 are three different nozzles used in this work. 4L4 nozzle has wider barrel curvature compared to 4L0 nozzle which has straight long barrel. This geometry of nozzle in 4L4 results in higher velocity of powder than in 4L0, this leads to less amount of time for powders to be in the nozzle, so powders would finally have lower temperature than powders that pass from 4L0. 4L2 nozzle in intermediate condition compared to both 4L4 and 4L2. This means that the temperature and velocity of the powders that are processed by 4L2 nozzle would be in a range between the temperature and velocity of powders that are processed by 4L4 and 4L0. Change in each of these parameters (nozzle and fuel-air ratio) can result in different velocity and temperature of powders. Effect of powder temperature and velocity on coatings property has been widely discussed in theoretical part of this thesis.

Table 19 shows the variable factors and their levels that are used for spraying 13 different coatings. As it can be seen, three different nozzle types have been used and fuel 1 and fuel 2 can each have two different values.

Table 18:Variable processing factors and their levels

Variables	Level		
	-1	0	1
X1=Nozzle type	4L0	4L2	4L4
X2=Fuel 1 (psi)	99		105
X3=Fuel 2 (psi)	90		105

Twelve different coatings will be produced by changing and combining these variable factors. In fact, for this process, a Full Factorial Experiment (FFE) has been employed. Table 20 presents the way that these twelve different coatings are produced by varying these factors together. In fact these three different variable factors can be assumed as three different axles of a cube. For example, nozzle type can be assumed as axle X and Fuel 1 as axle Y and Fuel 2 as axle Z of the cube. In this case axle Y and Z would each have two levels and axle X would have 3 levels. In fact, combination of these variable factors result in twelve different conditions. As a result, there would be totally 12 specific points on the sides of this cube. By considering this cube, it would be realized that the point with the characteristic of Fuel 1: 102 (psi) or .703 MPa, Fuel 2: 97.5 (psi) or 0.672 MPa and nozzle type 4L2 locates in the middle of the cube. Three more coatings were sprayed by using the same factors of this central point. The reason for three times spraying a coating with the same factors is to evaluate the reliability and repeatability of the spraying process. This act of repetition is called replication which has an advantage that allows the experimenter to get a more precise estimate of the experimental error. So all in all, 15 coatings, 13 different types, were sprayed.

Table 19: The way of producing 12 different coatings by changing variables

run	X1	X2	X3
1	-1	-1	-1
2	-1	-1	1
3	-1	1	-1
4	-1	1	1
5	0	-1	-1
6	0	-1	1
7	0	1	-1
8	0	1	1
9	1	-1	-1
10	1	-1	1
11	1	1	-1
12	1	1	1

In the DOE terminology, a trial or run is a certain combination of factor levels whose impact on the output is interesting to be understood. [88]

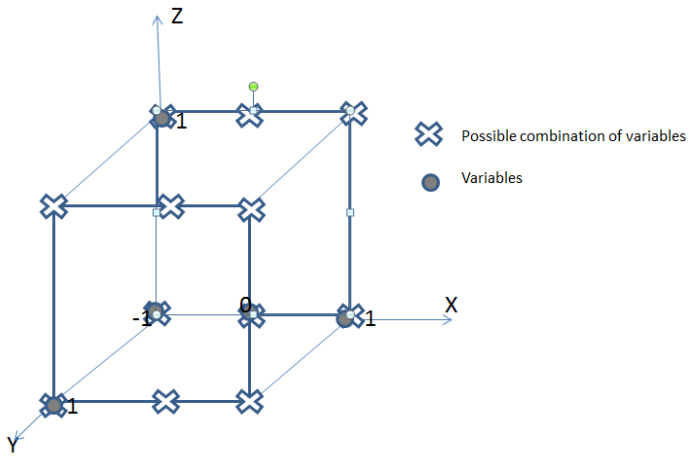


Figure 37: Cube representing the variables and their possible combination

The highest fuel-air ratios were chosen in a way so that powders could be processed with all the nozzle types. The lowest fuel-air ratios were chosen so there would be a significant difference with the highest fuel-air ratio. This brings the opportunity for evaluating the effect of fuel-air ratio on the obtained properties of the coating. The middle fuel-air ratios used in this project are between the maximum and minimum ratio and in the middle of the cube.

The results of the experiments are presented in the next sections and in the final step the Minitab 15 statistical software is used for analyzing the data. The idea is to understanding the effect of these variable factors on the obtained properties of the coatings and finding out the optimum factors that result in the desired property.

7.1.3 Characterization techniques

In this work, different characterization methods were used to study the coated samples. At the beginning, all the coating sample bars were cut by Struers cutting machine. Some of the samples were then mounted in cold resin by hot mounting method. In the next step, cross sections were grinded and polished metallographically to be prepared for optical microscopy, and also microhardness measurements. Other samples were also cut from each bar for other different experiments such as open cell corrosion test, roughness measurement, rubber wheel abrasion test and XRD.

Optical microscope (Materials microscope system Leica DM 2500) was used to take pictures of coatings and also measuring thickness of the coatings by Leica software. The Vickers micro hardness (1 kg and 300 gr) was measured on cross sections using MMT-X7 MATSUZAWA with load duration of 10 s. Roughness of the coatings were examined by portable Mitutoyo roughness tester after eight measurements. Phase composition was assessed by X-Ray Diffractometry (XRD, Empyrean, PANAnalytical, Cu-Kα radiation).

Wear resistance of the coatings was also tested by rubber wheel abrasion test device located in wear center labs at Tampere University of Technology. The quartz sand (0.1-0.6 mm) was fed between the rotating rubber wheel and coating samples while the coatings were pressed against the rubber wheel. 5 kg weights were used for pressing the coating sample surfaces to the rotating rubber wheel. The total time of the wear test was 60 minutes.

Open circuit potential (OCP) test was done for evaluating the corrosion behavior of all the coatings. The open circuit potential is the potential of the working electrode (Coatings and substrate in this case) relative to the reference electrode when no potential or current is being applied to the cell. The solution used for this experiment was water with 3.5 wt. % NaCl. This solution resembles the sea water which is indeed a really corrosive environment. Each coating was exposed to this environment for 336 hours and its potential was measured compared to the reference electrode by passing the time. The idea in this test is evaluating the amount of time that coating can protect the substrate by not letting the corrosive solution to pass it. In fact, when the corrosive electrolyte reaches the substrate or gets near to it, the potential of the working electrode changes.

7.2 Results and Discussion

In this section of the experimental work, obtained results from microstructure, micro hardness measurement, roughness measurement, open cell corrosion test, wear test and X-ray diffraction will be discussed and presented.

7.2.1 Microstructure

Figures 38-52 show the optical micrographs of the samples. However some coatings are more porous than the others but almost all coatings generally look dense and compact. Defects like vertical or horizontal cracks do not exist in the coating microstructures. It basically shows that the coatings processing has been done in a good way and chosen parameters are in a practical acceptable range.

As it can be observed, coating 119 looks a bit different compared to other coatings. In fact, some black stripes can be seen in this coating. These black stripes can be duo to the accumulation of a phase in the coating. For example, it may be possible that hard carbides have been accumulated together during the processing so they are seen as black veins in the coating. EDX microanalysis can be useful for realizing the composition of these black veins. The author of this thesis suggests (EDX) microanalysis to be done in the next stages of the project for deeper understanding of the composition and phase distribution in the coatings.

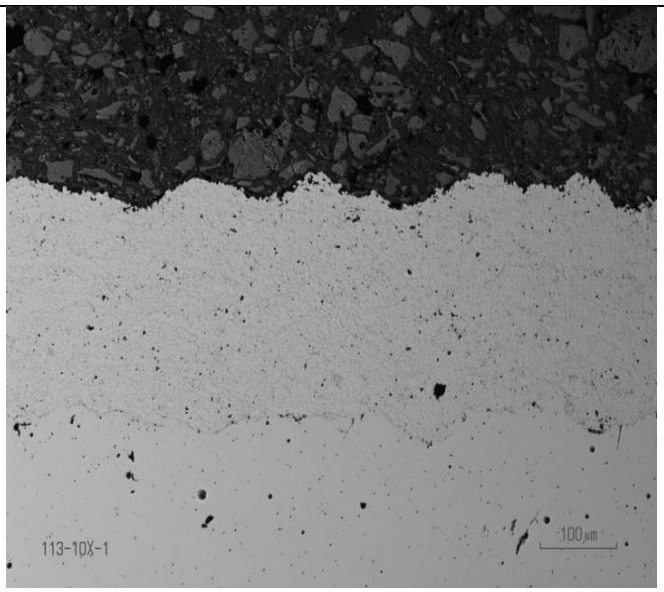


Figure 38:Optical micrograph of coating 113

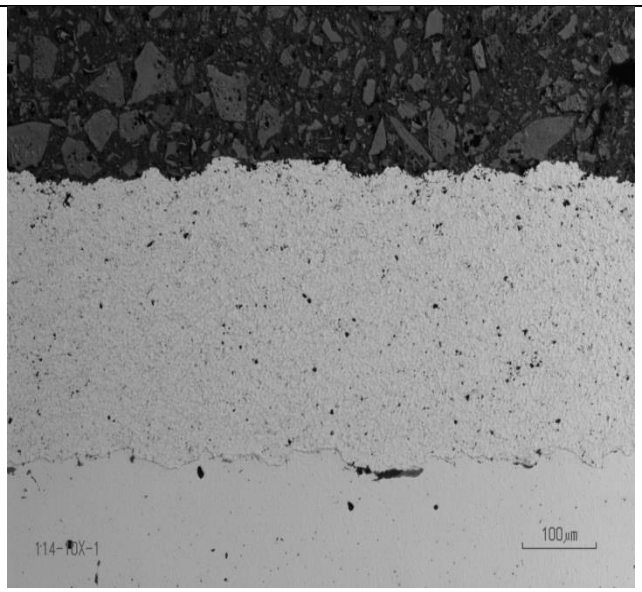


Figure 35:Optical micrograph of coating 114

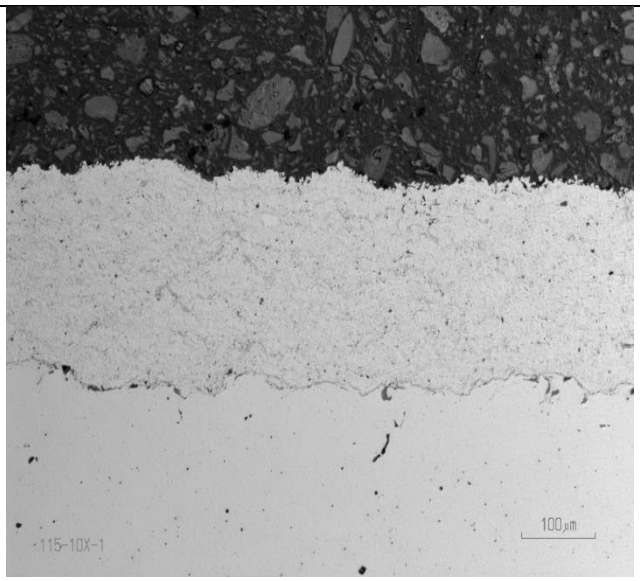


Figure 40:Optical micrograph of coating 115

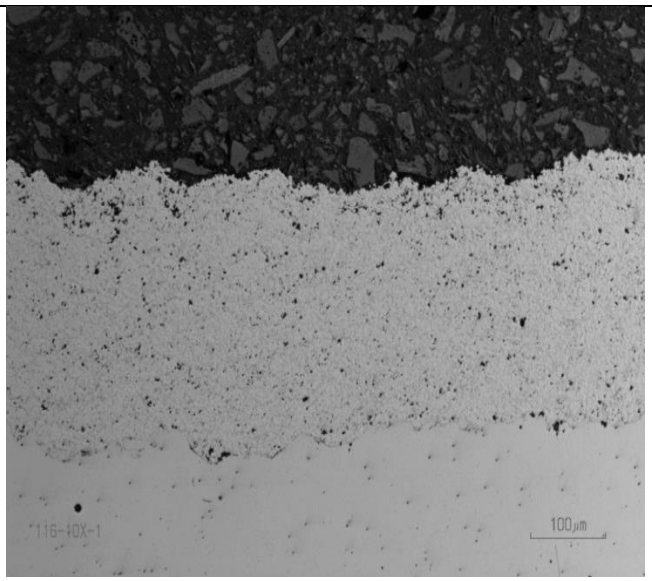


Figure 41:Optical micrograph of coating 116

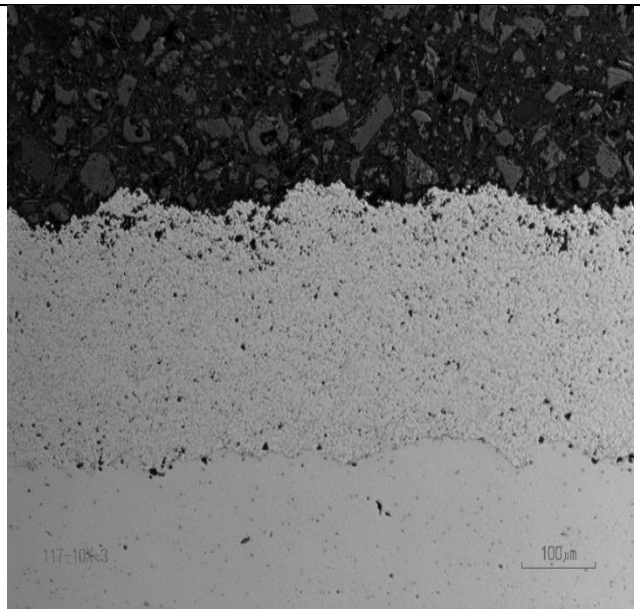


Figure 42:Optical micrograph of coating 117

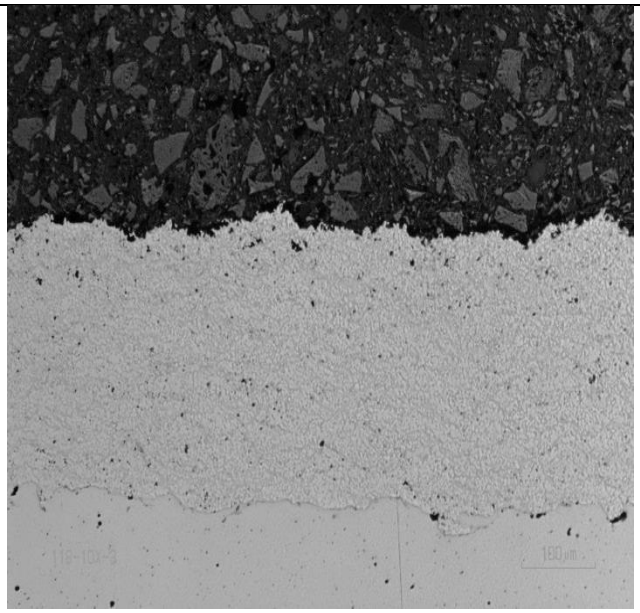


Figure 43:Optical micrograph of coating 118

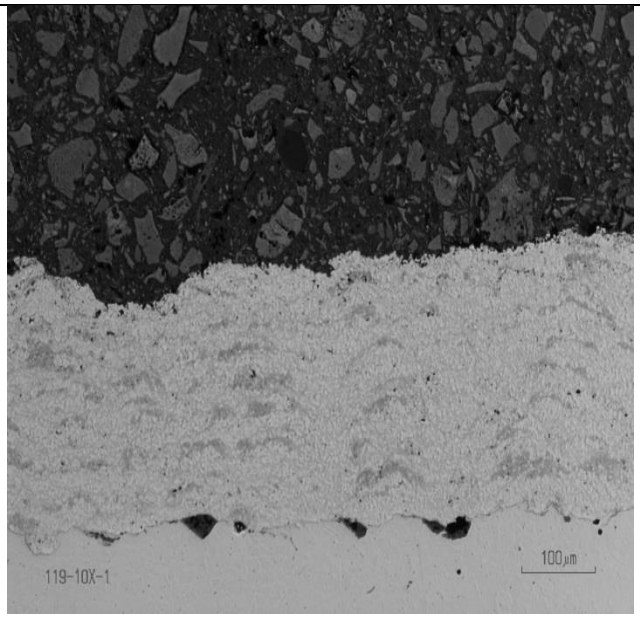


Figure 44:Optical micrograph of coating 119

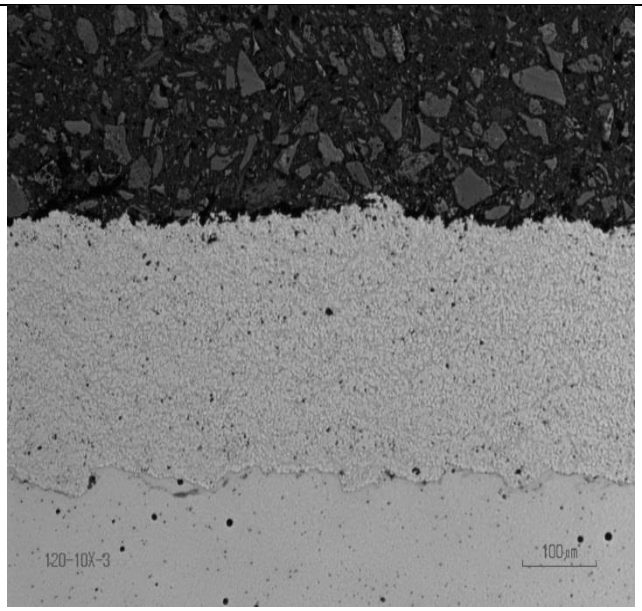


Figure 45:Optical micrograph of coating 120

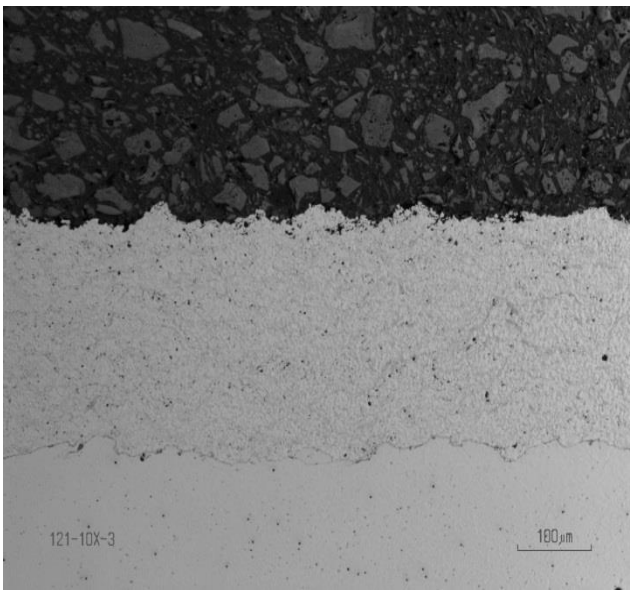


Figure 46:Optical micrograph of coating 121

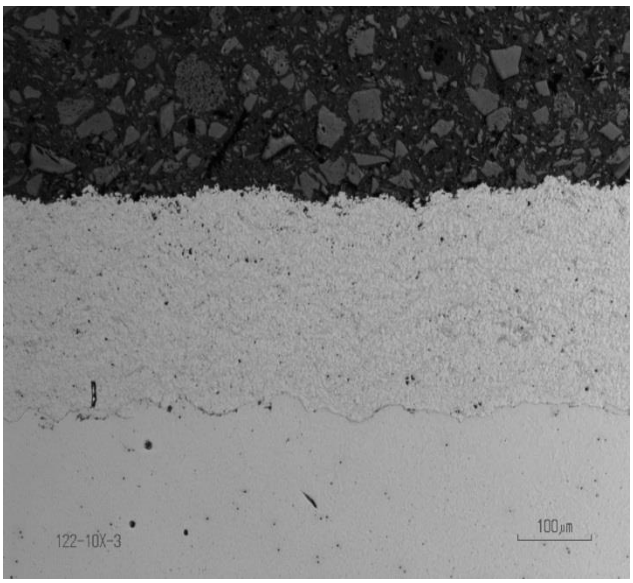


Figure 47:Optical micrograph of coating 122

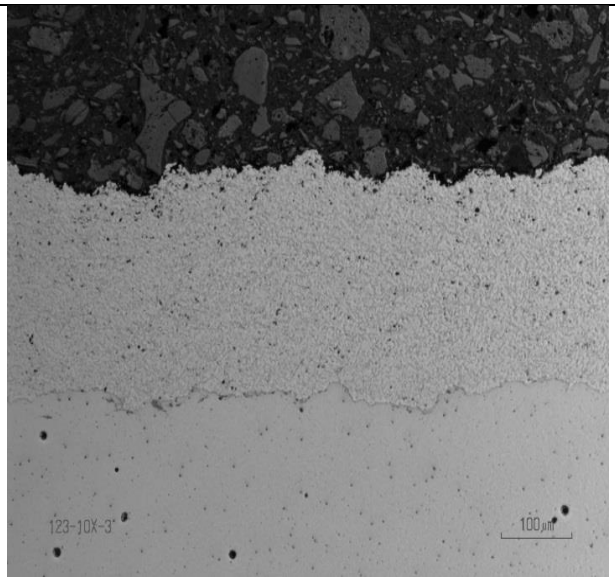


Figure 48:Optical micrograph of coating 123

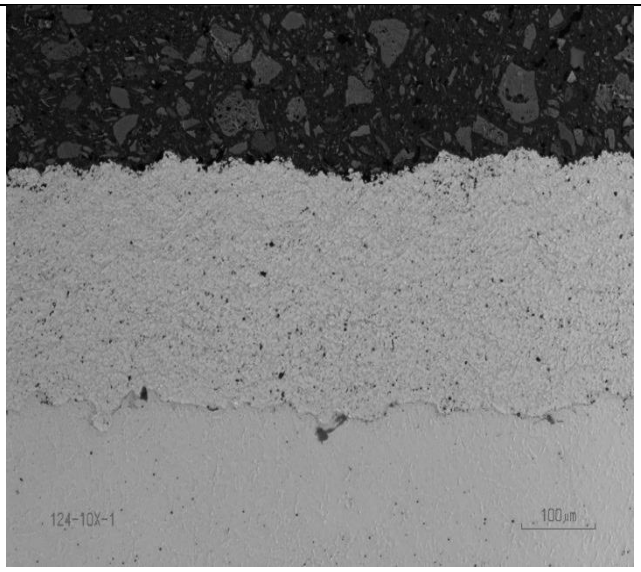


Figure 49:Optical micrograph of coating 124

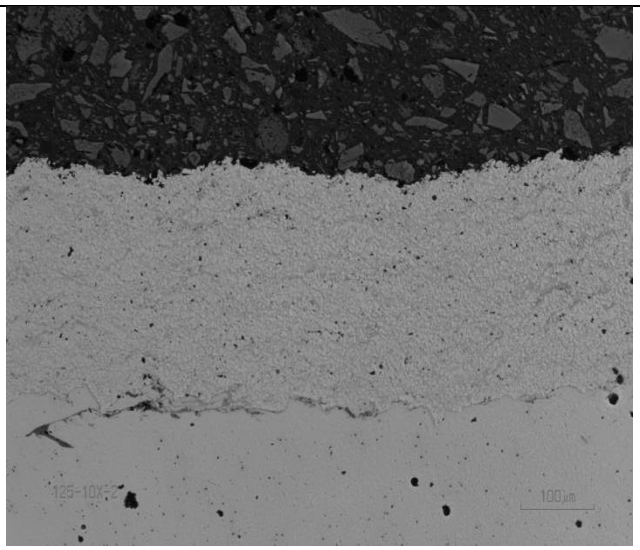


Figure 50:Optical micrograph of coating 125

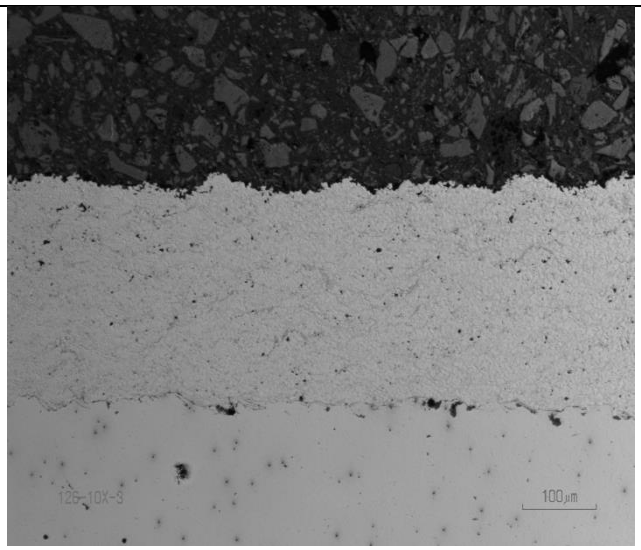


Figure 51:Optical micrograph of coating 126

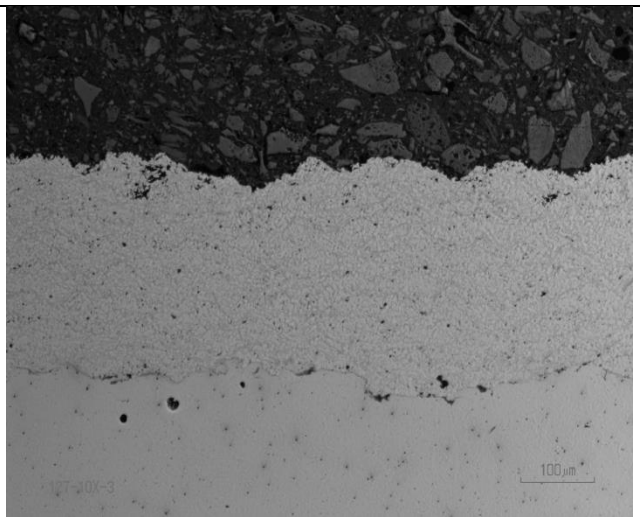


Figure 52:Optical micrograph of coating 127

Amount of porosity in the coatings was measured by Image J. A summary of porosity measurement is presented in table 21 and figure 53.

Table 20:Summary of the porosity measurements

Coating	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127
Porosity %	0.602	0.421	0.515	0.877	1.186	0.553	0.226	0.393	0.318	0.249	0.420	0.285	0.381	0.281	0.333

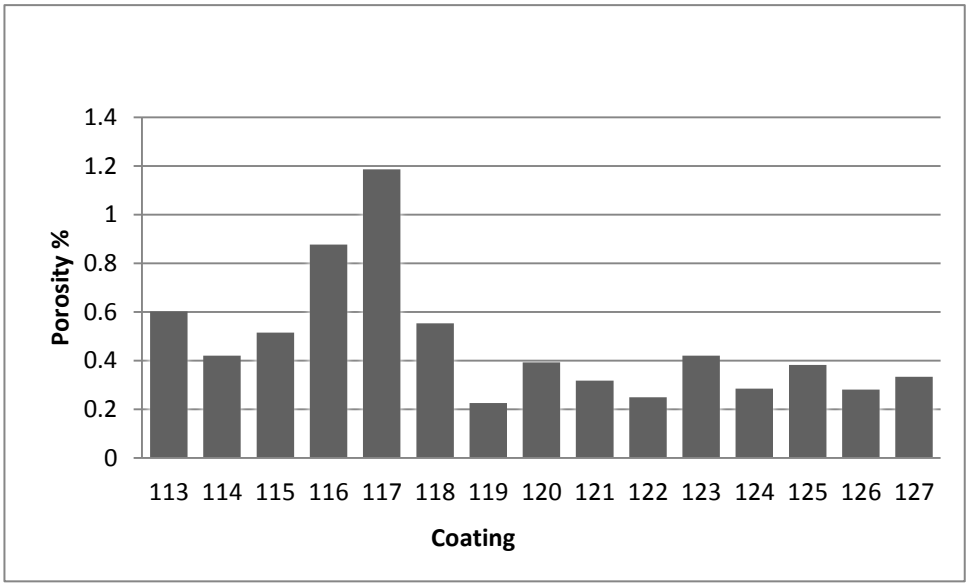


Figure 53: Comparison of porosity in coatings

The usual amount of porosity is less than 1% in HVAF process and around 1-2 % for HVOF process. Based on the results, the amount of porosity in almost all coatings is less than the usual amount of porosity (1%) for HVAF thermal spraying processes. It means that the selected processing parameters for this project and powder are appropriate. Interesting point is that coatings 116 and 117 have the highest amount of porosity and as it can be seen in the next section (hardness results); they have the lowest hardness compared to other coatings. This is also correct for coating 119; this coating has the lowest amount of porosity and possesses one of the highest amounts of hardness in all coatings. It can be realized that appropriate amount of velocity and heat in the process results in denser coating with high cohesion and it means higher hardness.

7.2.2 Microhardness

Table 22 and figure 54 represents the mean microhardness (10 measurements) and standard deviation values of each sample under 300 gr (~3 N) load.

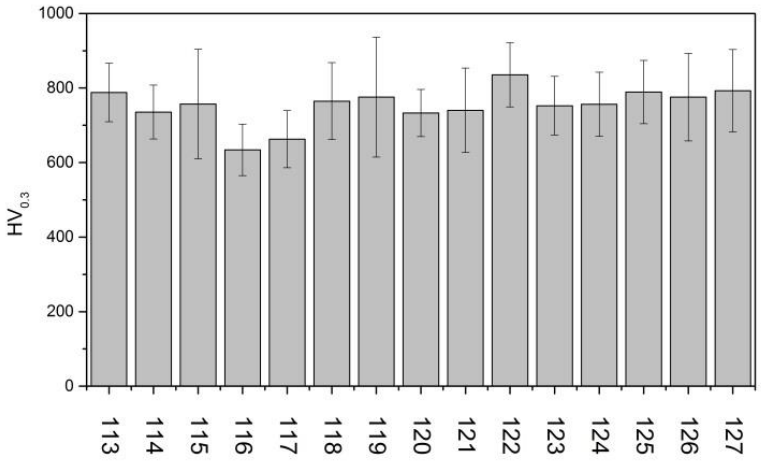


Figure 54:Vickers microhardness comparison of the coatings

Table 21: Vickers micro hardness and standard deviation of the coatings measured under 300 gr load.

Coating	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127
HARDNESS ($HV_{0.3}$)	788	735	756	633	662	764	775	733	740	835	752	756	789	775	792
STANDARD DEVIATION	78	72	146	69	76	103	161	63	113	85	78	85	84	117	110

As it can be observed, generally coatings show high standard deviation of hardness. Actually coatings are consisted from two different phases inside their composition, hard carbide phase and austenite phase. The difference in the hardness of these two phase result in the deviation in the measured hardness of the coating.

Mean hardness of the coatings was measured again with 1 Kg (~10 N) load with the aim of lowering the measured hardness deviation in the coatings. Table 23 represents the obtained results.

Table 22: Vickers micro hardness and standard deviation of the coatings measured under 1 Kg load.

Coating	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127
HARD-NESS(HV_1)	738	718	776	560	574	760	777	704	754	822	706	776	787	751	768
STANDARD DEVIATION	42	42	64	52	53	62	84	54	74	47	33	48	58	38	46

As it can be seen, mean measured hardness of the coatings show less deviation after the usage of 1 Kg (~10 N) load in the hardness test. In fact, using higher load leads to larger area of pin contact on the surface of the coating. This results in simultaneous consideration and measurement of both phases in the coating during each hardness test. As a result, the deviation from the mean hardness would be lower when 1 Kg (~10N) load is used compared to 300 gr (~3N) load during the hardness tests.

Results of both sets of hardness measurements exhibit that most of the coatings have approximately high hardness, above 700 Vickers. This shows that by using appropriate processing parameters, one can achieve hard coatings with this novel powder. Another considerable point is that, although various range of processing parameters are used to deposit coatings but most of the coatings exhibit high hardness and roughly in the same range. This means that this novel powder is not so sensitive to processing parameters which is a really good advantage for industrial applications.

7.2.3 Thickness of the coating

Table 24 exhibits the measured thickness of the coatings. Thicknesses were measured by using the scale bars of the photos in a specific magnification. Ten thickness measurements were done in different positions of every coating and mean thickness was calculated for each coating in the next step.

Table 23:Mean thickness of the coating, thickness per pass and standard deviation of measured thickness for each pass.

Coating	**113**	**114**	**115**	**116**	**117**	**118**	**119**	**120**	**121**	**122**	**123**	**124**	**125**	**126**	**127**
Thickness (µm)	252	324	229	292	271	302	285	285	262	245	230	270	271	270	251
Thickness per pass (µm)	31	32	38	32	33	37	35	31	32	30	28	30	33	33	31
Standard deviation of thickness per pass (µm)	1.6	1.06	3.2	1.3	1.6	2.3	2.7	1.6	1.2	1.6	1.4	1.5	2.5	1.04	1.7

Thickness per pass can be a decisive factor for estimating the efficiency of coating processing. If other parameters affecting the deposition are kept constant, which is the case in this study, then the higher thickness of the coating obtained in each pass of the thermal spraying processing means that the higher would be the processing efficiency. It means that less amount of powder is wasted and more amount of powder is deposited on the substrate in each pass. The reason is that, the amount of powder used for all set of processing parameter is the same.

The number of spraying passes is already known, so thickness per pass can easily be calculated by dividing the final thickness of each coating by its number of spraying passes. The following figure demonstrates the result of the calculations for each coating.

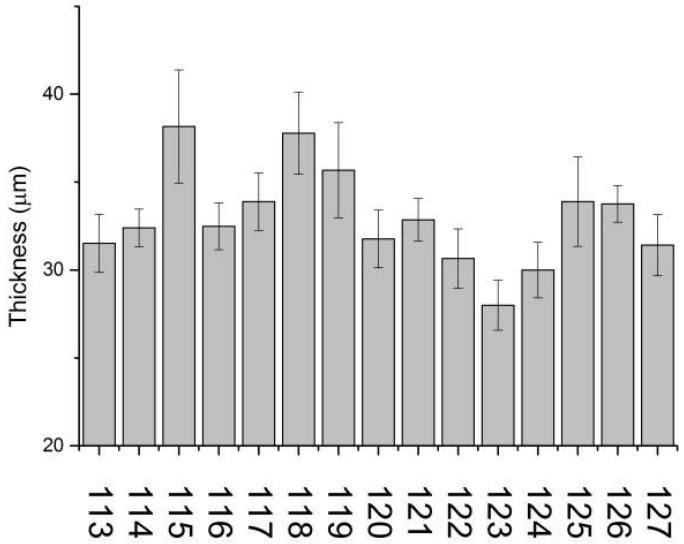


Figure 55: Thickness per pass comparison for coatings and their standard deviations

As it can be concluded from the above figure, parameters used during the spraying of 115 and 118 coatings have resulted in higher efficiency in these coatings compared to the other ones.

7.2.4 Roughness

Roughness plays a significant role on how a real object will interact with its surrounding environment and it would affect the wear mechanism considerably. Lack of homogenity in size distribution of the lamellae, non-flattened particles and surface defects could make the coating rougher.

Roughness of the coatings was examined by portable Mitutoyo roughness tester after eight measurements for each coating sample. The mean roughness and its deviation from this mean value was calculated for each coating. The results are presented in the following table and figure.

As it can be observed from figure 56, values of the roughness for all the coatings are in the same range except for coating 119 which has higher roughness compared to other coatings.

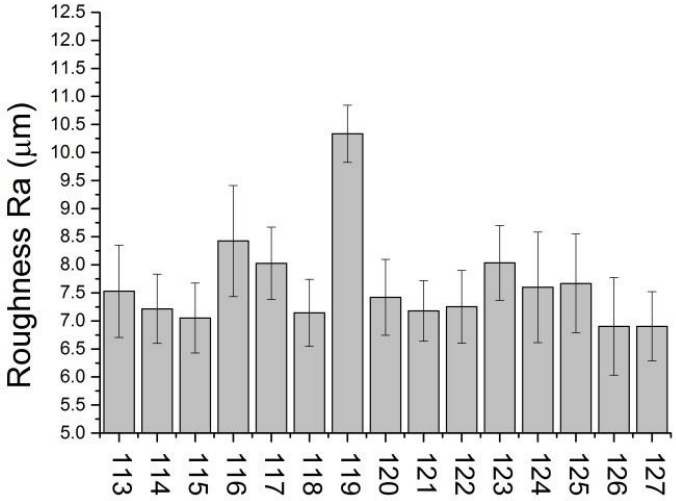


Figure 56: Roughness measurements

Table 24: Roughness measurements:

Coating	**113**	**114**	**115**	**116**	**117**	**118**	**119**	**120**	**121**	**122**	**123**	**124**	**125**	**126**	**127**
Roughness R_a(µm)	7.5	7.21	7.05	8.42	8.02	7.14	10.33	7.42	7.17	7.25	8.03	7.59	7.66	6.90	6.90
Standard deviation of Roughness R_a(µm)	0.82	0.61	0.62	0.98	0.64	0.59	0.50	0.67	0.53	0.64	0.66	0.98	0.88	0.86	0.61
Roughness R_z(µm)	48.07	51.39	47.77	54.92	50.82	47.63	64.34	49.79	46.10	47.73	52.28	48.88	48.75	45.20	45.94

7.2.5 Phase compositions of coatings

Figure 57 presents diffraction patterns of the sprayed coatings. XRD difraction peaks show that all the coatings have the same phase composition; however they are produced by using different processing parameters. In fact M_7C_3 and $M_{23}C_6$ (M can be Fe or Cr) make the composition of the hard phases and austenitic steel is the composition of the remained phase in coatings.

Comparison of the obtained XRD diffraction peaks from coatings and used powder (page 86) shows that the composition in all coatings and powder is similar. During coating formation and processing, no carbide dissolution or phase change (decarburization, interphases with austenite, oxidation) has occurred.

As it is mentioned before, the hard carbide phase is consisting of compositions of Iron carbide and chromium carbides. Iron carbide has the melting point of 1600 $^{\circ}$C and chromium carbides has the melting point of 1900 $^{\circ}$C. This high melting point of these phases prevents them to be totally melted during HVAF thermal spraying process. In addition, the lower temperature of HVAF thermal spraying processes compared to other thermal spraying methods result in hindering of the possible phase changes such as decarburization and oxidation. This is a big advantage for HVAF thermal spraying processes because using this process results in preservation of the powder phase and composition. This advantage is well observed in this thesis project.

The only change in composition of coatings compared to the powder is the slight change occurred in austenite phase. This can be duo to different reasons such as strong plastic deformation that occurs during coating formation or melting of this phase during processing. Because the temperature and velocity of powders are not known, so the exact reason of this change is not clear. Also peak broadening of the austenite phase can be the result of grain refinement, microstrain, super saturated solid solution, or some amorphisation.

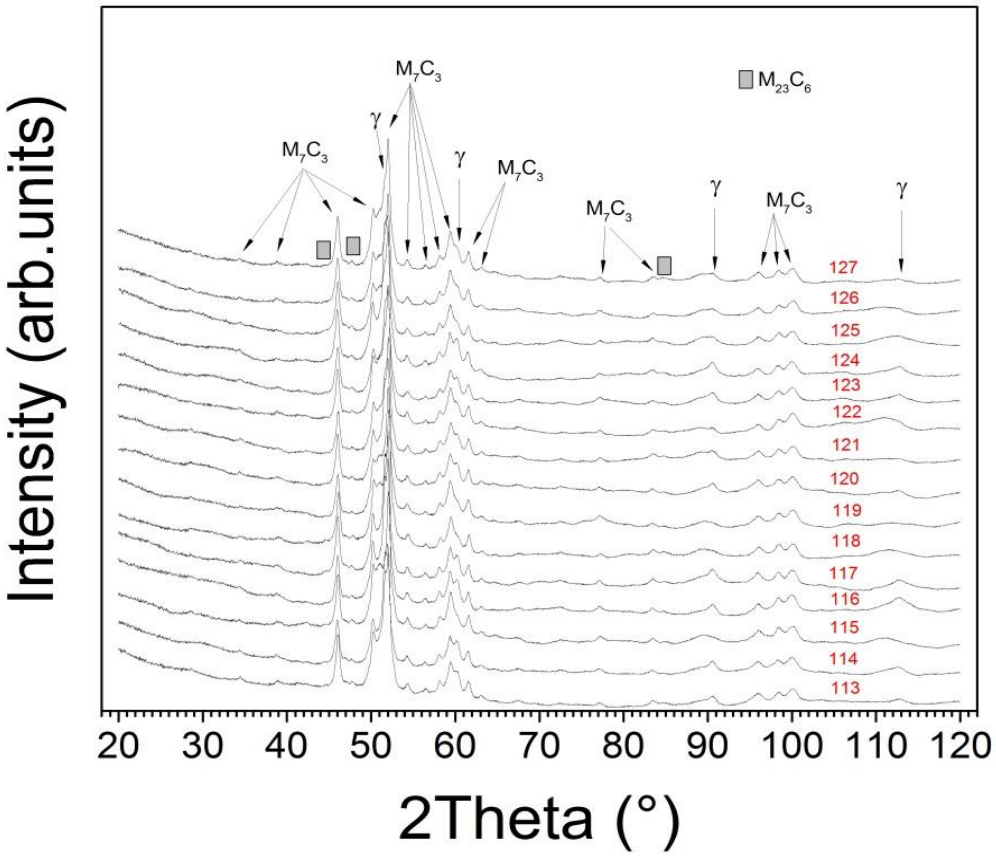


Figure 57: Diffraction patterns of the sprayed coatings

7.2.6 Wear resistance

Rubber wheel abrasion test was used for evaluating the wear resistance of the coatings. The quartz sand was fed between the rotating rubber wheel and coating samples while the coatings were pressed against the rubber wheel. 5 kg weights were used for pressing the coating sample surfaces to the rotating rubber wheel. The initial weight and the weight of the samples were measured every twelve minutes. The total length of experiment was 1 hour for each sample and three samples were tested for each coating type. In the next step the average value was calculated for each coating type in each time period.

Carbon steel samples were tested in addition to coating samples during the rubber wheel abrasion test. In fact, carbon steel was used as reference material and the wear resistant behavior of the coatings were compared with it.

Figure 58 compares the final weight loss of all coating types and reference.

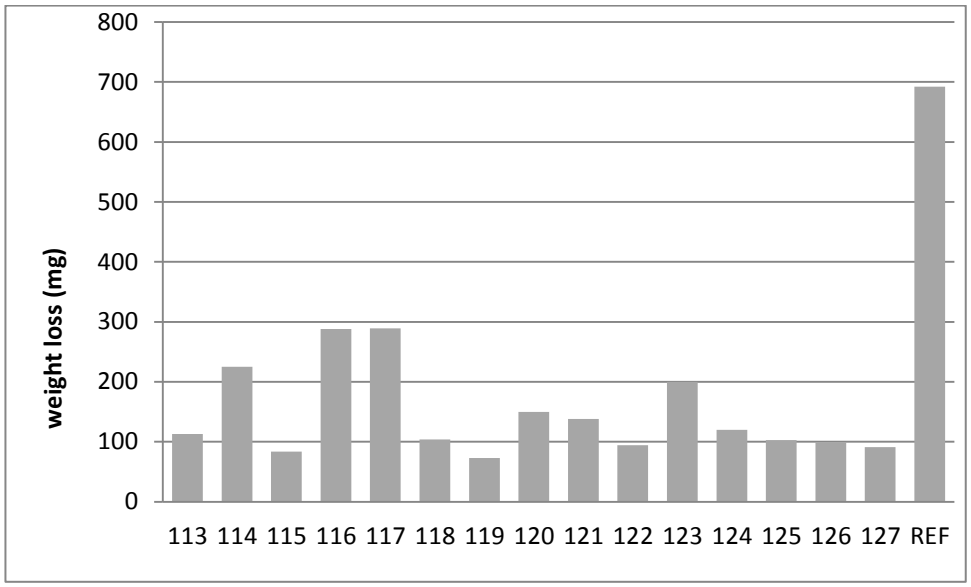


Figure 58: Wear loss after rubber wheel abrasion test

The following table represents the average weight of samples in each mentioned time for all types of coatings.

Table 25:Rubber wheel test results

Sample	0 min (g)	12 min (g)	24 min (g)	36 min (g)	48 min (g)	60 min (g)	Final weight loss (mg)
113	153.295	153.275	153.246	153.226	153.202	153.182	113
114	155.515	155.467	155.42	155.38	155.341	155.290	225
115	153.560	153.539	153.524	153.510	153.493	153.476	83.7
116	155.922	155.878	155.830	155.765	155.699	155.634	288
117	154.546	154.492	154.43	154.376	154.326	154.257	289
118	154.281	154.258	154.237	154.219	154.198	154.177	104
119	150.825	150.812	150.798	150.785	150.767	150.752	73
120	155.068	155.047	155.018	154.982	154.947	154.918	150
121	155.201	155.171	155.141	155.115	155.093	155.063	138
122	154.393	154.372	153.354	154.338	154.321	154.299	94.3
123	156.123	156.09	156.056	156.014	155.968	155.924	200
124	153.354	153.334	153.311	153.283	153.257	153.234	120
125	155.567	155.543	155.525	155.506	155.490	155.463	103
126	156.99	156.971	156.953	156.935	156.916	156.894	99
127	155.837	155.822	155.806	155.787	155.765	155.746	91
REF	148.409	148.248	148.112	147.973	147.829	147.716	692

As it can be concluded from the results in the worst case which is related to the coating 117, the wear shows a decrease of 58.2 percent compared to the reference material which is a carbon steel without any additional coating layer. In the best case which is related to coating 119, the wear rate has decreased 89.4 percent. It means that almost all of the coatings have successfully decreased the amount of wear compared to the substrate without any coating. This is a promising result for Amperit 575 novel powder to be processed by high velocity air-fuel thermal spraying (HVAF) for applications where they are involved by 3 body abrasion wear.

In addition, results show that coatings 116 and 117 show the highest amount of wear and coating 119 shows the lowest amount of wear. Actually coatings 116 and 117 have the lowest value of hardness (560-574 HV respectively) between all the coatings and coating 119 has a really high hardness of 777 HV. As it was mentioned during the theoretical part, hardness of the coating has significant role on abrasion wear. In fact high hardness and elasticity are main factors that can control and decrease the abrasion wear rate.

Regression analysis shows that there is a strong correlation between the mean hardness values (measured with 1 Kg load) and final weight loss of the coatings in this project. Calculations show that the correlation coefficient between these two factors is approximately -0.85. It means that increasing hardness in coatings has resulted in lower final wear loss.

These results show that wear loss has opposite relation with the mean hardness in coatings. So as a result, efforts should be focused to find out processing parameters that cause producing coatings with highest possible hardness. For example in this project, processing parameters used for producing coating 119 seems promising for the used powder and as it can be seen this coating has the highest hardness and the lowest amount of porosity between all other coatings. On the other hand processing parameters used for producing coatings 116 and 117 does not seem to be appropriate.

Of course the role of the elasticity of the coatings should never be neglected. In fact, H/E ratio has a decisive role in the wear property of the coatings as it is discussed in the theoretical part. Increasing the hardness without considering the elasticity of the coating can result in brittleness of the coating which is detrimental.

7.2.7 Open-cell potential test

Open-cell potential test was done for evaluating the corrosion behavior of all the coatings. The open-cell potential is the potential of the working electrode (coatings and sub-

strate in this case) relative to the reference electrode when no potential or current is being applied to the cell. The solution used for this experiment was deionized water with 3.5 wt.% NaCl solution. This solution resembles the sea water which is indeed a really corrosive environment. Each coating was exposed to this environment for 336 hours and its potential was measured compared to the reference electrode by passing the time. The idea in this test is evaluating the amount of time that coatings can protect the substrate by not letting the corrosion potential to get more negative.

It should be noted that the coating´s material (70 (Fe,Cr)C / 30 FeNiCrSi) is nobler compared to the substrate which is low carbon steel. This is duo to the composition of the coatings, carbide phase is the main constituent of these coatings, this makes them nobler compared to the substrate which is low carbon steel. It should be mentioned that some powders were also immersed in the 0.61 molar NaCl solution for understanding the corrosion behavior of the powders. During 336 hours of immersion, they did not corrode at all. It exhibits that these powders have a great potential to resist against corrosion.

Results of the test shows that by passing time, the measured potential of all coating types gets more negative in a fast trend. This means that the corrosive solution penetrates the coatings and the substrate feels this penetration and the relative potential which is measured compared to the reference electrode gets more negative. This means that unfortunately these coatings are not successful for stopping the solution to penetrate to the substrate. This can be due to the existence of connected pores or cracks in the coating that lets the corrosive solution to pass from it and get near the substrate or even reach it. So in fact the powders have high potential to resist corrosion but the processing of the coatings should be upgraded to prevent the solution to pass from the coatings. Indeed, coatings are relatively dense but there are some open porosities which is seen in the open-cell potential measurements. Getting SEM microstructural photos is recommended for obtaining more clear idea about the microstructure of the coatings.

The following figure represents the result of the Open circuit (oc) potential tests of all the coatings.

As it can be seen in all the coatings, the corrosion potential drops down dramatically in a short period of time and the potential reaches to around -500 mV which is near to the relative potential of the substrate that is around -650 mV. Of course in some coatings, it is observed that in some points the corrosion potential gets nobler. This is probably duo to the formation of some nobler compounds in the coating which are produced during the corrosion process. But this trend is not stable and finally the corrosion potential again starts to drop down.

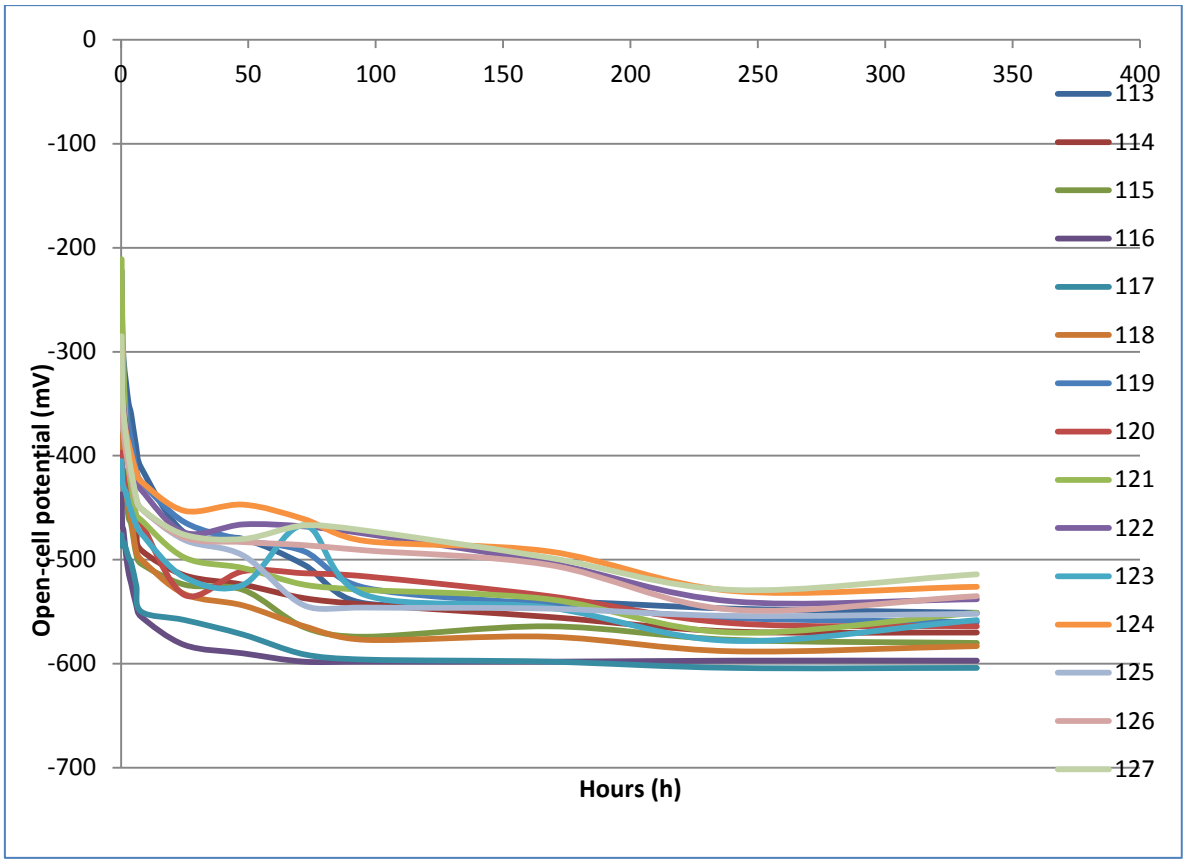


Figure 59:Open-cell potential curves for all coatings.

Abundance of pits on the surface of all the coatings after this experiment shows that pitting is a serious corrosion mechanism and these coatings are prone to this mechanism. In addition, some reddish corrosion products can be observed on the surface of the coatings. It is assumed that these are the corrosion products of the substrate material that come on the surface and deposit. EDX microanalysis or electron spectroscopy analysis of these corrosion products can lead us to find out the real nature of these deposits and also the prevalence of coating´s or substrate´s corrosion.

Figure 60: Opticel stereoscopy photos of coatings 118 (left) and 115 (right) after corrosion test.

7.3 DoE analysis and discussion

Minitab 15 statistical software is used for analyzing the gained data. The idea is to understanding the effect of variable factors on the obtained properties of the coatings and finding out the optimum factors that result in the desired property.

Based on the design of the experiment (DOE), $Fuel_1$ and $Fuel_2$ pressure and also nozzle type are among the variable factors during thermal spraying process of the coatings. As it is discussed previously, $Fuel_1$ and $Fuel_2$ each have two levels but nozzle type has three levels. Porosity, hardness, roughness and wear rate are considered among the experimental results. So the idea is to find out the effect of variable factors on these results and to analyze how the change of these factors affects the property and performance of the coatings. For example, it can be found out that what are the optimum processing factors that should be chosen for producing coatings with specific hardness or wear rate. It is important to note that not all the factors affect the performance in the same manner. Some may have strong impacts, some may have medium impact and some others have no influence. Furthermore, interaction between the factors was also studied and analyzed in this report. Interaction occurs when the effect of one process parameter is dependent on the level of the other process parameter. The existance of the interaction between two parameters can be understood from the interaction plot of those two parameters. If the lines in the plot are parallel to each other, it means that there is no interaction between those two parameter. If the lines are not parallel then there is interaction between the parameters and it basically means that effect of one process parameter is dependent on the level of the other process parameter.

It should be mentioned that Open-cell potential test is not considered between the results and the reason is that generally these coatings do not show good corrosion behavior. In fact these coatings exhibit high hardness and low wear rate which makes them good candidates for applications where wear phenomena is involved. As a result, the focus of analysis is concentrated on optimization of the variable processing factors for producing coatings with high hardness and low wear rate.

7.3.1 Porosity

Porosity response versus levels of different factors (nozzle type, fuel1, fuel2) is shown in the figures 61 and 62. As it can be seen, different levels of each factor has impact on the mean porosity of coatings. For example if it is desired to have coatings with the lowest possible amount of porosity, then using nozzle 4L2 is recommended. Or increasing the Fuel 1 ratio leads coatings to have less porosity but on the other hand it can be observed that increasing fuel 2 ratio results in higher amount of mean porosity in coatings.

But it is also interesting to determine whether two factors are interacting or not. As it is mentioned before, interaction occurs when the effect of one process parameter is dependent on the level of the other process parameter.

Porosity response versus levels of two factors can be observed from figure 62.

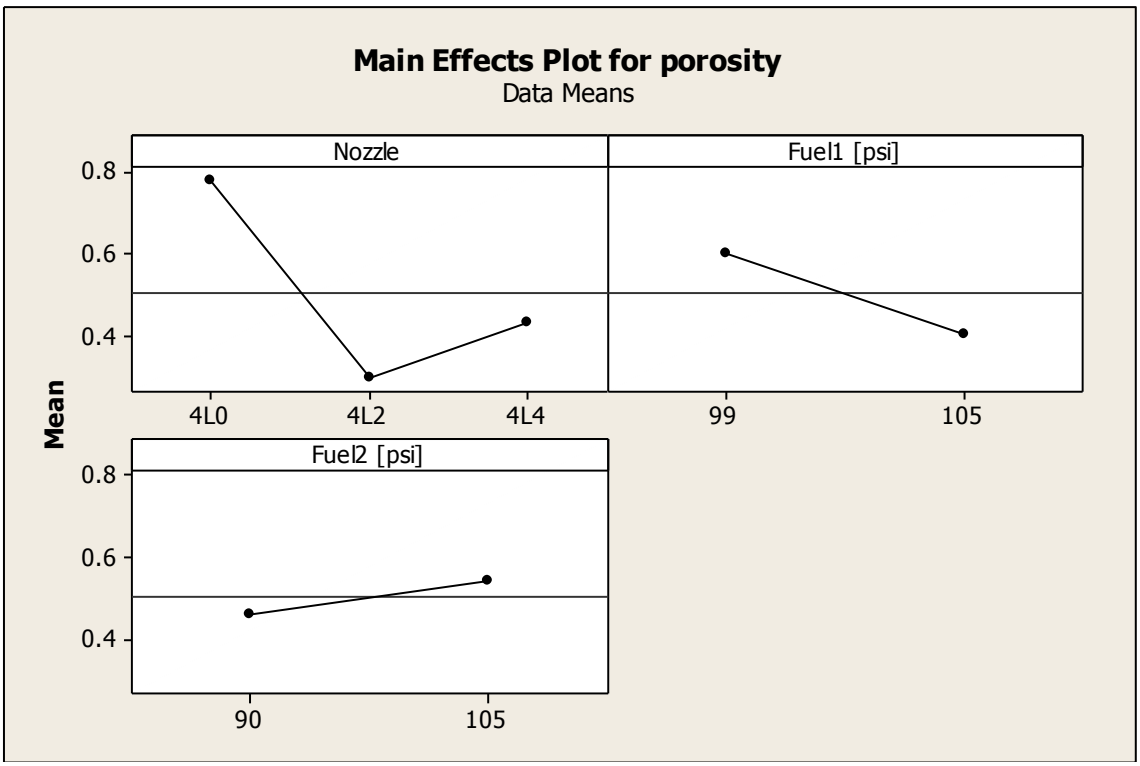


Figure 61:Porosity response versus levels of one factor

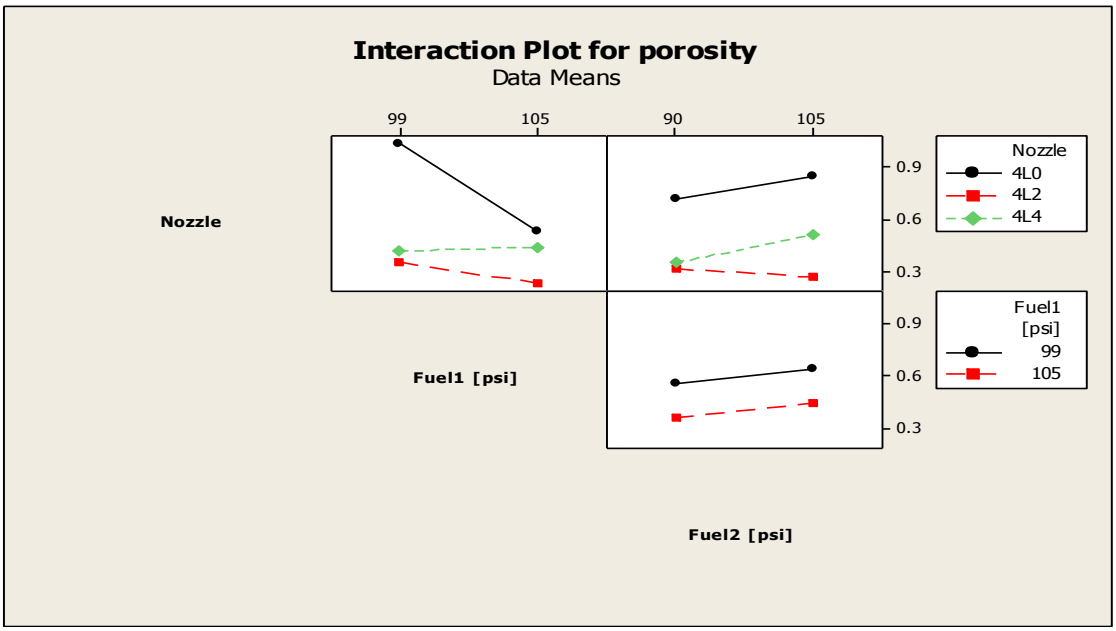


Figure 62: Interaction plot for porosity

In the case of porosity, there is no interaction between fuel 2 and fuel 1 because the lines in the interaction plot are parallel. This implies that the change in the mean response of porosity from low to high level of the fuel 2 does not depend on the level of the fuel 1. The interaction graph between fuel 2 and nozzle type shows that there is an interaction between these two factors. The porosity is minimum when the fuel 2 level is at high level and nozzle 4L2 is used. The interaction between other factors can also be determined from figures.

7.3.2 Roughness

The following figures present the main effects plot for roughness and the interaction plot.

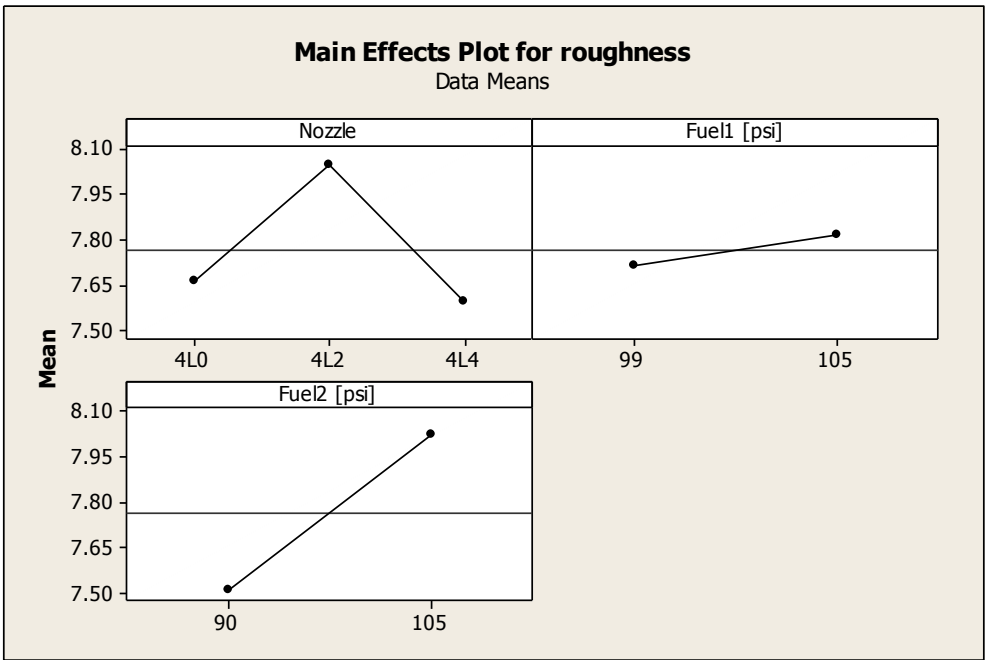


Figure 63: Roughness response versus levels of 1 factor

The highest possible roughness can be obtained by applying high level of fuel 2 and keeping other factors constant. This is the same for fuel 1 while other factors are kept constant. In case of changing nozzle type, using nozzle 4L2 result in the highest amount of roughness while other factors are constant.

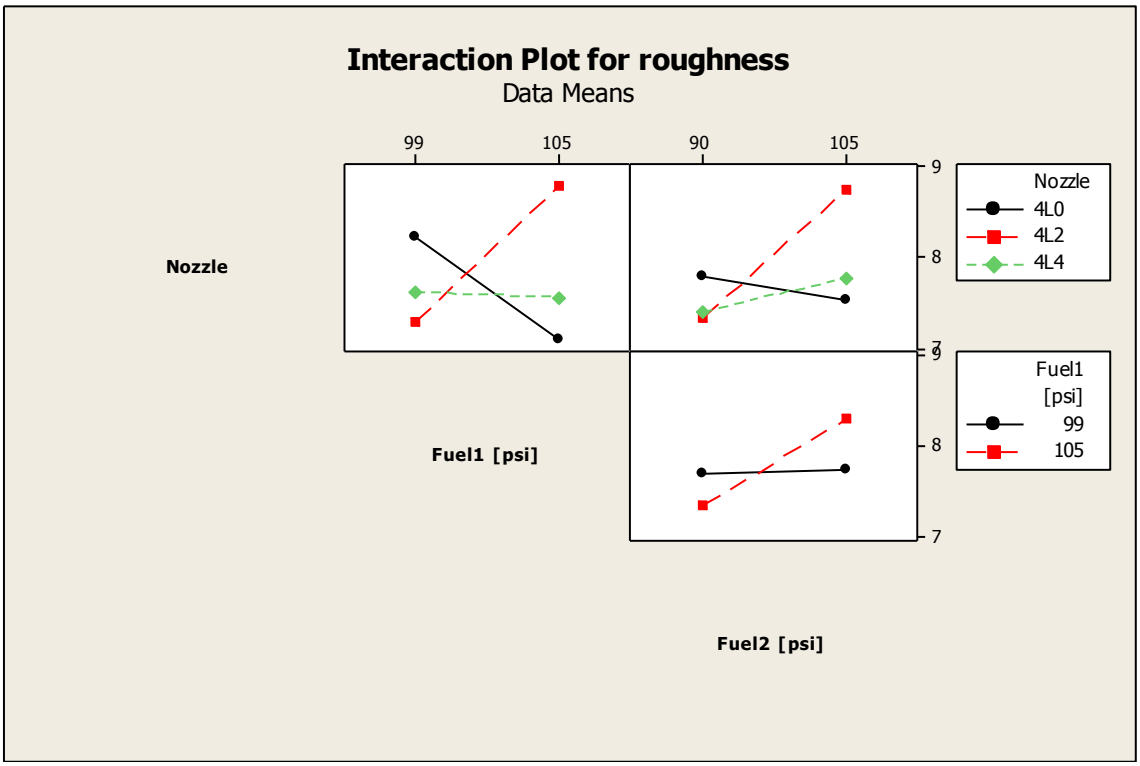


Figure 64: Interaction plot for roughness

Based on the interactions in the plots of figure 64, it can be concluded that fuel 1 and fuel 2 have interaction. Of course fuel 1 and nozzle type, fuel 2 and nozzle type have also interaction but their interactions are not discussed here. The minimum amount of roughness in coatings are obtained by applying low level of fuel 2 and high level of fuel1. The interaction between other factors can also be determined from figures.

7.3.3 Hardness

As it is discussed in previous sections, hardness of the coating is one of its important properties that affect its performance. As a result it is important to determine and optimize the processing factors so the desired value for the hardness of the coatings can be gained. As it is mentioned already, nozzle type, fuel1 and fuel 2 are amongst the processing factors that are variable. Their effects on hardness and their interactions are discussed here.

Based on the plots that can be observed in the figure 65, Hardness of the coatings increase if fuel1 is increased to higher level. Of course other factors are kept constant. Or if fuel 1 and nozzle type are chosen and are kept constant, then hardness again increases insignificantly by increasing the fuel 2 level. In another scenario, fuel 1 and fuel 2 levels can be kept constant and nozzle type be changed. In this case, nozzle 4L2 should be chosen to obtain coatings with the highest possible hardness.

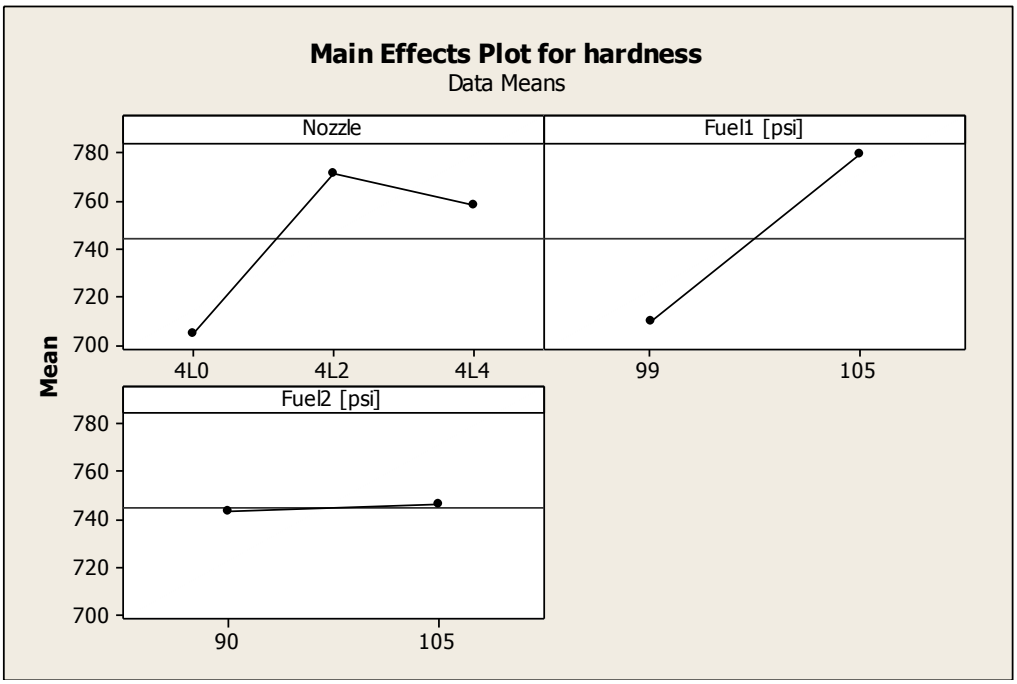


Figure 65: Hardness response versus levels of 1 factor

Figure 66 exhibits the interaction plots for two involved factors. In this case, we are interested to see the impact of simultaneous change of two parameters on the hardness of the coating. Two scenarios are possible, if the variable factors interact each other or not.

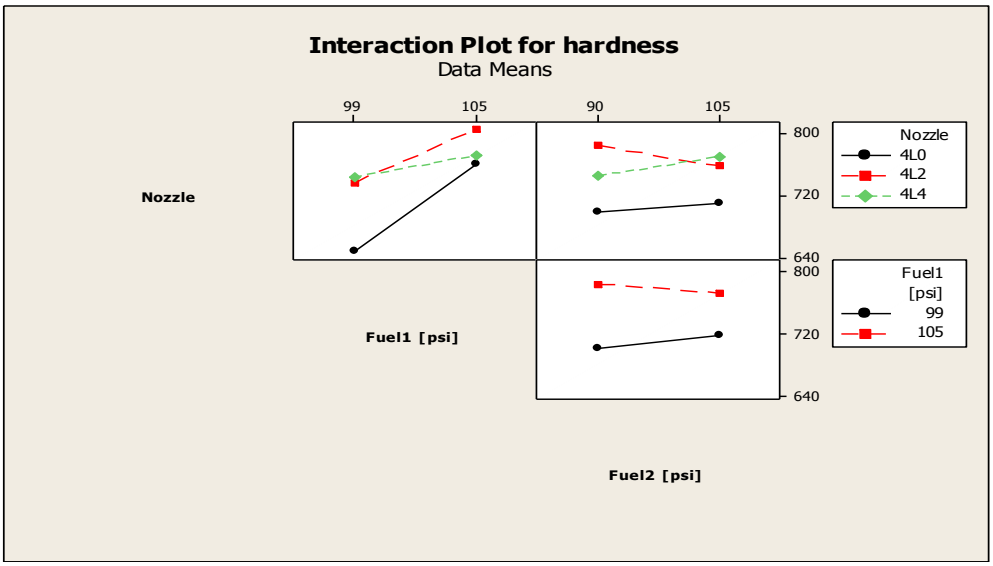


Figure 66: Interaction plot for hardness

As it can be seen from the above figure, an interaction can be observed between fuel1 and fuel 2 because their lines are not parallel. Of course, the deviation of hardness values should also be considered. The mean value of hardness would be maximum when fuel 2 is in low level and fuel 1 is increased to high level. It means that in a specific case where nozzle type is chosen, then the maximum mean hardness can be obtained by

using low level of fuel 2 and high level of fuel 1. The interaction between other factors can also be determined from figures and plots.

7.3.4 Wear loss

As it is explained and discussed already, resistance against wear is indeed the main application of the coatings that are studied in this project. As a result it is important to decrease the final amount of the wear in coatings. In fact, processing factors should be analyzed and optimized to improve the quality of the coatings. DOE analysis can be used as powerful tool for determining the processing factors that lead in production of coatings with minimum amount of wear loss. The effects of variable factors on wear loss and their interaction are discussed here for the produced coatings in this project.

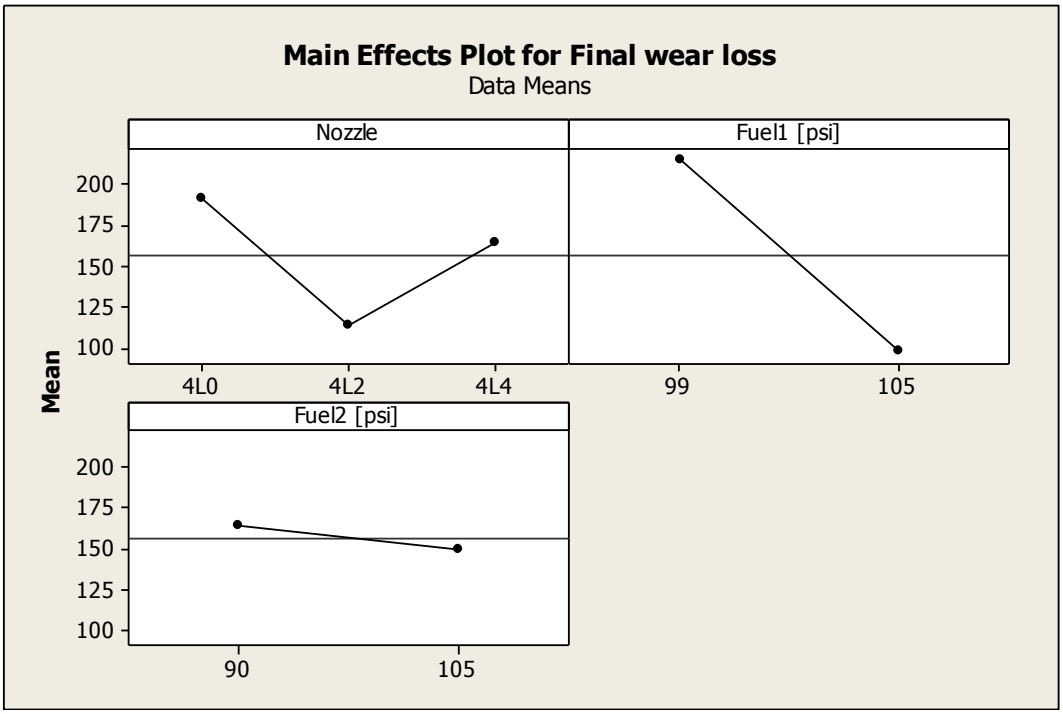


Figure 67: Wear loss response versus levels of 1 factor

As it can be concluded from the above figure, increasing the fuel 1 level can result in the decrease of the mean wear loss value. Of course other variable factors should be kept constant. Trend is the same for using fuel 2 as variable and keeping other factors constant. In addition using nozzle 4l2 can result in lower wear loss amount compared to coatings that are produced by other nozzle types, by considering other factors constant.

Figure 68 represents the results of the interaction of the factors on the wear loss of the coatings. As it can be seen from the interaction plot of fuel1 and fuel2, these factors

basically do not show any interaction because the lines are parallel. It means that the change in mean wear loss response from low to high level of fuel 2 does not depend on the level of the fuel 1 factor. Wear loss is minimum when the level of the fuel 2 and fuel 1 is increased. The interaction between other factors can also be determined from figures and plots.

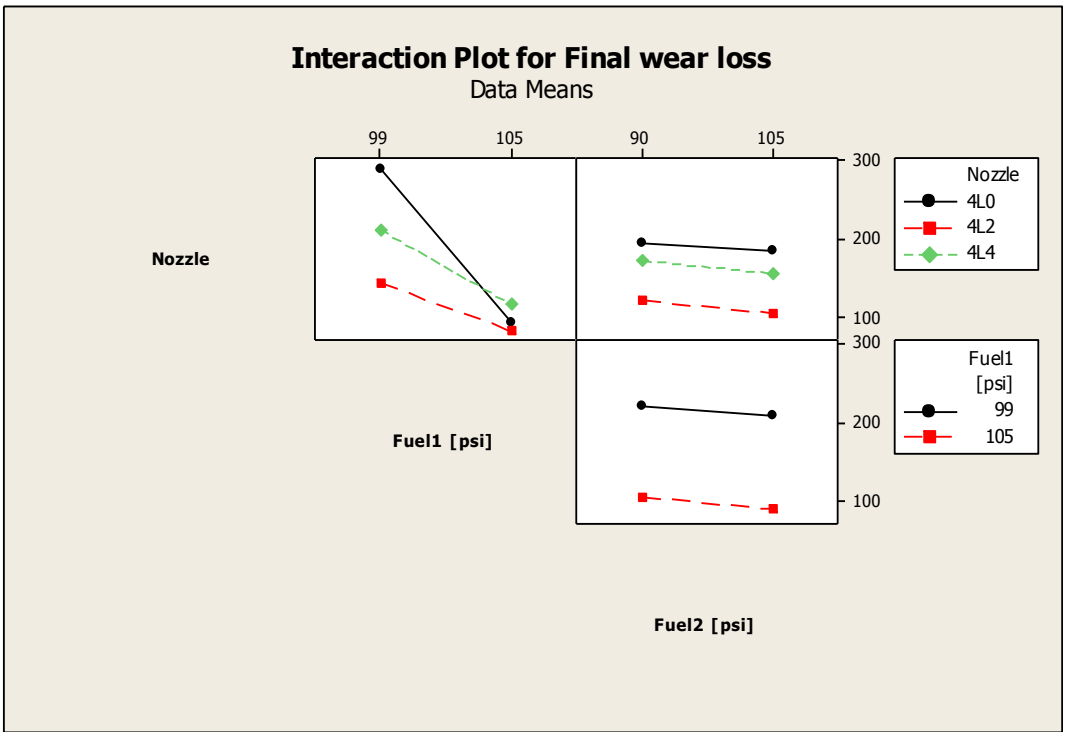


Figure 68: Interaction plot for final wear loss

8. CONCLUSIONS

This research focused on Design of Experiment (DoE) of a novel cermet coating sprayed with the HVAF technology onto steel substrates.

In the first phase of the research, DOE as a useful technique for planning, analyzing and exploring the processes was used for designing the experiment. Based on the DOE; air pressure, spray distance, carrier gas, step size, powder feeding rate were among the factors that were kept constant during the thermal spraying of powders. On the other hand, nozzle type and fuel1 and fuel2 amounts were chosen to be variant factors. Twelve different types of coatings, fifteen coatings totally, were sprayed with the HVAF technology by applying designed processing factors.

In the second step, the obtained coatings were characterized. Their microstructural features, micromechanical properties, abrasive wear behavior and corrosion properties were studied as a function of the process parameters and were compared to the characteristics of each other. The main conclusions of this study are as follows.

Optical micrographs of the samples prove that although some coatings are more porous than the others but almost all coatings generally look dense and compact. Defects like vertical or horizontal cracks are not common in the coating microstructures. It basically shows that the coatings processing has been done in a good way and chosen parameters are in a practical acceptable range.

Based on the results, the amount of porosity in almost all coatings is less than the usual amount of porosity (1%) for HVAF thermal spraying processes. It means that the selected processing parameters for this project and powder are appropriate. Interesting point is that coatings 116 and 117 have the highest amount of porosity and as it can be seen from hardness results; they have the lowest hardness compared to other coatings. This is also correct for coating 119; this coating has the lowest amount of porosity and possesses the highest amount of hardness in all coatings.

Results of hardness measurements exhibit that most of the coatings have approximately high hardness, above 700 Vickers. This shows that by using appropriate processing parameters, one can achieve hard coatings with this novel powder. Another considerable point is that, although various range of processing parameters are used to deposit coatings but most of the coatings exhibit high hardness and roughly in the same range. This means that this novel powder is not so sensitive to processing parameters which is a really good advantage for industrial applications.

As it can be concluded from thickness measurements, parameters used during the spraying of 115 and 118 coatings have resulted in higher efficiency in these coatings compared to the other ones. Based on the roughness measurements, values of the roughness for all the coatings are in the same range except for coating 119.

Comparison of the obtained XRD diffraction peaks from coatings and used powder (page 86) shows that the composition in all coatings and powder is quite the same. During coating formation and processing, no carbide dissolution or phase change (decarburization, interphases with austenite, oxidation) has occurred. The only change in composition of coatings compared to the powder is the slight change occurred in austenite phase. This can be duo to different reasons such as strong plastic deformation that occurs during coating formation or melting of this phase during processing. Because the temperature and velocity of powders are not known, so the exact reason of this change is not clear. Also peak broadening of the austenite phase can be the result of grain refinement, microstrain, super saturated solid solution, or some amorphisation. In fact it can be generally concluded that the amount and types of the phases in the coatings are the same with the powder and the characteristics of the powder is preserved during the processing.

Based on the results of the abrasion wear test, in the worst case which is related to the coating 117, the wear shows a decrease of 58.2 percent compared to the reference material which is a carbon steel without any additional coating layer. In the best case which is related to coating 119, the wear rate has decreased 89.4 percent. It means that almost all of the coatings have decreased substantial amount of wear compared to the material without any coating layer. This is a promising result for Amperit 575 (70 (Fe,Cr)C / 30 FeNiCrSi) novel powder to be processed by high velocity air-fuel thermal spraying (HVAF) for applications where they are involved by 3 body abrasion wear.

The corrosion potential drops down dramatically in a short period of time and the potential reaches to around -500 mV which is assumed to be the relative potential of the substrate. This means that unfortunately these coatings are not successful for stopping the solution to penetrate to the substrate. This can be duo to the existence of connected pores or cracks in the coating, as a result of using powders with non-optimized size, that lets the corrosive solution to pass from it and get near the substrate or even reach it. Of course, it should be considered that NaCl solution is a really aggressive corrosive. Getting SEM microstructural photos is recommended for obtaining more clear idea about the microstructure of the coatings.

In last phase of the research, Minitab 15 statistical software was used for analyzing the gained data. The idea was to understand the effect of variable factors on the obtained properties of the coatings and finding out the optimum factors that result in the desired property. It is important to note that not all the factors affected the performance in the

same manner. Some had strong impacts, some medium impact. Furthermore, interaction between the factors was also studied and analyzed in this report.

The promising results obtained for Amperit 575 novel powder, processed by high velocity air-fuel thermal spraying (HVAF) proves the urgent for further studies on this material and process. More micromechanical test such as, sliding wear and cyclic impact resistance should be done on these coatings for deeper understanding of their mechanical properties. In addition, obtaining SEM photos and EDS microanalysis of the coating sound necessary for determining the coating properties.

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